



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : B01F 17/00, C11D 1/04, 1/12, 1/34		A1	(11) International Publication Number: WO 98/15345 (43) International Publication Date: 16 April 1998 (16.04.98)
(21) International Application Number: PCT/IB97/01230		(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(22) International Filing Date: 6 October 1997 (06.10.97)			
(30) Priority Data: 08/726,439 4 October 1996 (04.10.96) US			
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(54) Title: DETERGENT COMPOSITIONS CONTAINING LOW CONCENTRATION LEVELS OF GEMINI SURFACTANTS

(57) Abstract

Aqueous surfactant compositions containing low concentrations of surfactant actives are provided comprising a surfactant mixture with one or more gemini surfactants. The aqueous composition containing a total amount of surfactant based on active weight equal to or less than 0.01 % by weight based on the total weight of the composition. The gemini surfactants comprise from about 10 % to about 100 % by weight of the total surfactant active weight in aqueous composition.

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DETERGENT COMPOSITIONS CONTAINING LOW CONCENTRATION LEVELS OF GEMINI SURFACTANTS

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This invention relates to improved surfactant systems useful as emulsifiers and in detergents at very low concentration.

Emulsification is an extremely important technology and it is a process which 10 is used in detergency, emulsion polymerization, cosmetics, food, agrochemicals, paints, paper, transportation of crude oil, etc. Emulsifiers function as essential ingredients in personal care and household products; industrial and institutional cleaners including shampoo, car washes, carpet shampoo, hand dishwashing liquids, latex foaming and oil recovery compositions; and the like.

15 In order to form a relatively stable emulsion, an emulsifier is required to adsorb at an oil-water interface to prevent emulsion droplet coalescence. The majority of emulsifiers are synthetic surfactants or natural products with amphiphilic character. Presently, usage levels of surfactants for effective emulsification are usually above 0.1% active based on the total weight of the detergent solution which is used in the 20 final use composition. For a given emulsifier system, it would be advantageous to use a lower amount of surfactant to reduce the cost and amount of surfactant waste discharged into the environment; and to improve the performance of final products (e.g., the film forming and water resistance will be improved in latex paints and skin irritation will be reduced for cosmetic products with less surfactants).

While conventional surfactants generally have one hydrophilic group and one hydrophobic group, recently a class of compounds having at least two hydrophobic groups and at least two hydrophilic groups have been introduced. These have become known as "gemini surfactants" in the literature (Chemtech, March 1993, pp 30 - 33), 5 and J. American Chemical Soc., 115, 10083-10090, (1993) and the references cited therein). Other gemini surfactant compounds, that is, compounds having at least two hydrophilic groups and at least two hydrophobic groups are also disclosed in literature but often are not referred to expressly as gemini surfactants.

An intensive study of gemini surfactants as emulsifiers has been made. 10 From these studies, it has been found that gemini surfactants are unexpectedly effective emulsifiers when used at very low concentrations in comparison to conventional surfactants. This finding is reflected in superior detergency at very low concentrations. Other performance properties related to emulsification as mentioned above can be also improved using low concentrations of gemini surfactants.

15

SUMMARY OF THE INVENTION

In accordance with the present invention, it has been discovered that gemini surfactants of the type described and claimed herein can be extremely effective emulsifiers for oil-in-water emulsions at lower concentrations than that needed 20 utilizing corresponding conventional surfactants. Furthermore, the detergency is also improved over that provided by conventional surfactants at these low concentration levels.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1 and 2 are bar graphs representing the comparison of detergency of polyoxyethylene (13) methylene bis (octylphenol) (MBOP) versus a control of 5 polyoxyethylene (7.5) octylphenol (OP) on different fabrics at 0.005% & 0.01% by weight respectively.

Figures 3 and 4 are bar graphs representing the comparison of detergency of polyoxyethylene(13) methylene bis (octylphenol) (MBOP) in a 1:1 blend with sodium dodecylbenzene sulfonate versus a control of polyoxyethylene (7.5) octylphenol (OP) in 10 a 1:1 blend with the same sulfonate on various fabrics at 0.001% & 0.005% by weight respectively.

DETAILED DESCRIPTION OF THE INVENTION

The surfactant solutions of the invention are based on certain gemini surfactants.

15 As used herein, the term "gemini surfactants" is intended to mean surfactants having at least 2 hydrophobic groups and at least 2 hydrophilic groups per molecule.

A number of the gemini surfactants are reported in the literature, see for example, Okahara et al., J. Japan Oil Chem. Soc. 746 (Yukagaku) (1989); Zhu et al., 67 JAOCS 7.459 (July 1990); Zhu et al., 68 JAOCS 7.539 (1991); Menger et al., J. 20 Am. Chemical Soc. 113, 1451 (1991); Masuyama et al., 41 J. Japan Chem. Soc. 4.301 (1992); Zhu et al., 69 JAOCS 1.30 (Jan. 1992); Zhu et al., 69 JAOCS 7.626 July 1992); Menger et al., 115 J. Am. Chem. Soc. 2, 10083 (1993); Rosen, Chemtech 30 (March 1993); and Gao et al., 71 JAOCS 7.771 (July 1994), all of this literature incorporated herein by reference.

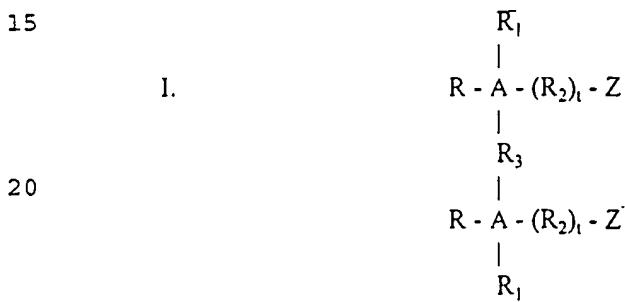
Also, gemini surfactants are disclosed by U.S. Patent Nos. 2,374,354, Kaplan; 2,524,218, Bersworth; 2,530,147 Bersworth (two hydrophobic tails and three hydrophilic heads); 3,244,724, Guttmann; 5,160,450, Okahara, et al., all of which are incorporated herein by reference.

5 The gemini surfactants may be anionic, nonionic, cationic or amphoteric. The hydrophilic and hydrophobic groups of each surfactant moiety (A, A') may be any of those known to be used in conventional surfactants having one hydrophilic group and one hydrophobic group.

For example, a typical nonionic gemini surfactant, e.g., a bis-polyoxyethylene 10 alkyl ether, would contain two polyoxyethylene alkyl ether moieties.

Each moiety would contain a hydrophilic group, e.g., polyoxyethylene, and a hydrophobic group, e.g., an alkyl chain.

Anionic and nonionic gemini surfactants which are useful in the present invention include those of the formula:



25 wherein R is independently C_1 to C_{22} alkyl, $R_4C(O) -$, or R_4-B-R_5-

wherein R_4 is C_1 to C_{22} alkyl, R_5 is C_1 to C_{12} alkyl, and B is an amide group.

[$-C(O)N(R_6)-$], an amino group [$-N(R_6)-$], a carboxyl group [$-C(O)-O-$], a carbonyl group, and a polyether group [$-O(EO)_nPO_2-$]

wherein EO represents ethyleneoxy radicals. PO represents propyleneoxy radicals. a and b are numbers of from 0 to 100, a is preferably from about 0 to about 30 and b is preferably from about 0 to 10, wherein a plus b is at least one, and the EO and PO radicals can be randomly mixed or in discrete blocks, and R₆ is hydrogen or C₁ to C₆ alkyl;

R₁ is independently hydrogen or C₁ to C₂₂ alkyl;

R₂ is independently a C₁-C₁₀ alkyl, -O-, an amide group [-C(O)N(R₆)-], a polyether group [-O(EO)_a(PO)_b-], -R₇-D-R₇- or

10. -D-R₇-D wherein R₇ is independently a C₁-C₆ alkyl and D is -O-, -S-, an amide group [-C(O)N(R₆)-], or an amino group [-N(R₆)-], wherein R₆, a and b are as defined above, and t is independently 0 or 1.

Z is independently hydrogen, -SO₃Y, -P(O)(OY)₂, -COOY, -CH₂COOY, -CH₂-CH(OH)CH₂SO₃Y and when R₂ is not a polyether, Z is also -OSO₃Y, and -15 OP(O)(OY)₂; wherein Y is hydrogen, alkali metal such as sodium and potassium; alkaline earth metal such as magnesium and calcium; ammonium; or organic base salt such as monoethanolamine, diethanolamine, triethanolamine, triethylamine, trimethylamine, N-hydroxyethyl morpholine, and the like.

A is independently a straight chain or branched C₁ to C₆ alkyl, such as

20. -CH-CH₂-, -CH-CH₂-, or -C-CH₂-,
| | |
| | |
CH₂ CH₂ CH₂

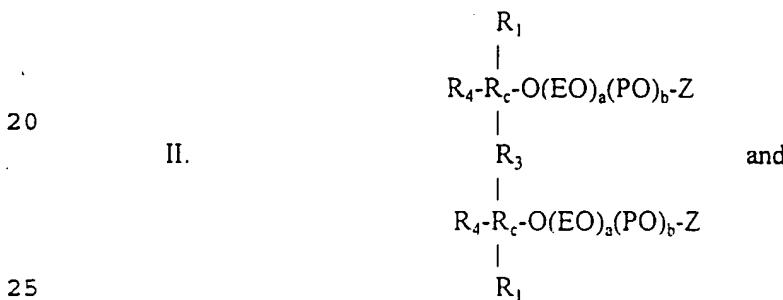
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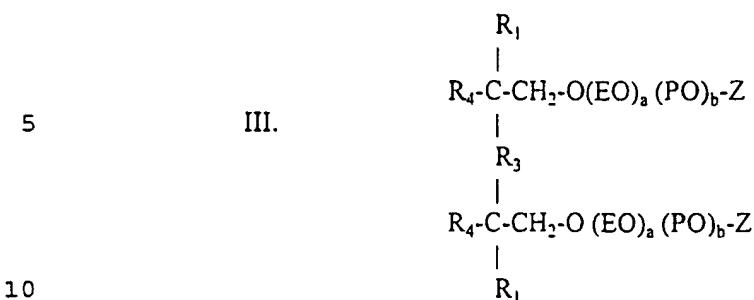
an O-R₅-O- group or aryl; preferably phenyl; R₃ is a bond, an aryl group such as a phenyl or diphenyl group, a C₁ to C₁₀ alkyl group, preferably a C₁ to C₄ alkyl group, most preferably methylene, -O-, -S-, -S-S-, -N(R₆)-, -R₅-O-, -R₅[O(EO)_a(PO)_b-], -D₁-R₈-D₁- or -R₈-D₁-R₈- wherein R₈ is independently a C₁-C₁₀ alkyl group, -C(O)-, 5 -R₅[O(EO)_a(PO)_b]-, -O-R₅-O-, or aryl, e.g. phenyl, and D₁ is independently -O-, -S-, -S-S-, -SO₂-, -C(O)-, a polyether group [-O(EO)_a(PO)_b-], an amide group [-C(O)N(R₆)-], an amino group [-N(R₆)-], -O-R₅-O-, or aryl wherein R₅, R₆, a and b are as defined above.

On the formulae of this disclosure, the term "alkali" includes substituted alkali, 10 especially the hydroxy substituted derivatives thereof and straight as well as branched chains. When Z is hydrogen, the gemini surfactants are nonionic.

The compounds of Formula I are more fully described in copending application U.S.S.N. 08/292,907 filed 08/19/94, the entire disclosure of which is incorporated herein by reference.

15 Other gemini surfactants specifically useful in the present invention include gemini anionic or nonionic surfactants of the formulae:



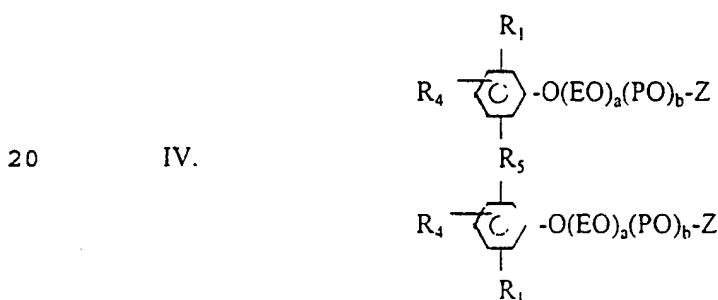


wherein R_c represents aryl, preferably phenyl.

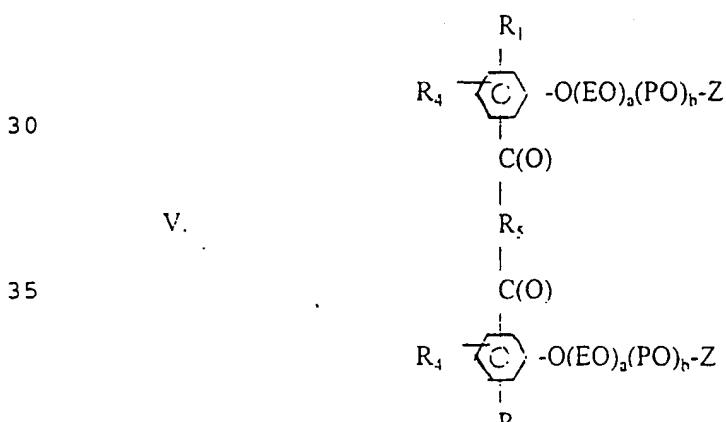
R_1, R_3, R_4, Y, Z, a and b are as defined above.

More specifically, these compounds comprise:

15



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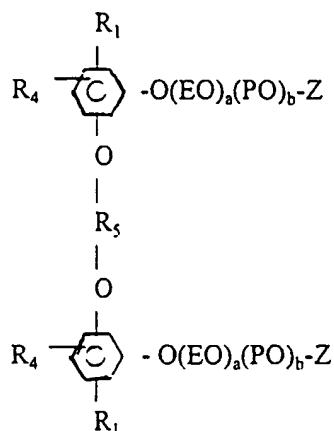


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VI.

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15 wherein R₁, R₄, R₅, Z, a, and b are as defined hereinbefore.

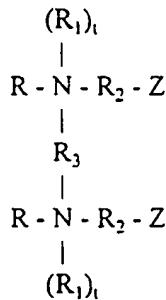
The primary hydroxyl group of these surfactants can be readily phosphated, sulfated or carboxylated by standard techniques.

The compounds included in Formula II can be prepared by a variety of synthetic routes. For instance, the compounds of Formula IV can be prepared by condensing a monoalkyl phenol with paraformaldehyde in the presence of an acid catalyst such as acetic acid. The compounds of Formula V can be synthesized by a Lewis acid catalyzed reaction of an alkylphenol with a dicarboxylic acid, e.g., terephthalic acid.

The compounds of Formula II are more fully described in copending application U.S.S.N. 60/009,075 filed 12/21/95, the entire disclosure of which is incorporated herein by reference.

A class of gemini surfactants that can be used in providing the improved emulsions which are operable at lower concentrations as disclosed in the present invention include a group of amphoteric, and cationic quaternary surfactants comprising compounds of the formula:

5 VII.



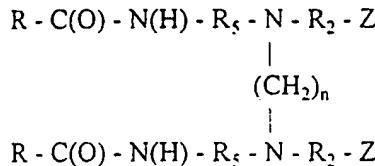
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wherein R, t, and Z are as defined hereinbefore. R_1 is as defined before and includes the $[-(EO)_a(PO)_bO-]H$ moiety. R_2 is as defined before, however, D includes the following moieties: $-N(R_6)-C(O)-R_5-CH_2O-$ and $-N(R_6)-C(O)-R_5-N(R_6)-R_4-$. When t is zero, the compounds are amphoteric and when t is 1, the compounds are cationic. 15 R_3 is selected from the group consisting of a bond, C_1-C_{10} alkyl, and $-R_8-D_1-R_8-$ wherein D_1 , R_5 , R_6 , a, b, and R_8 are as defined above (except R_8 is not $-OR_5O-$).

Preferably, the compounds of Formula VII comprise:

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VIII.

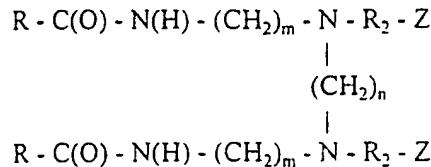


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wherein R, R_2 , R_5 and Z are as defined above and n equals a number from about 2 to about 10. More particularly, the compounds of Formula VII comprise:

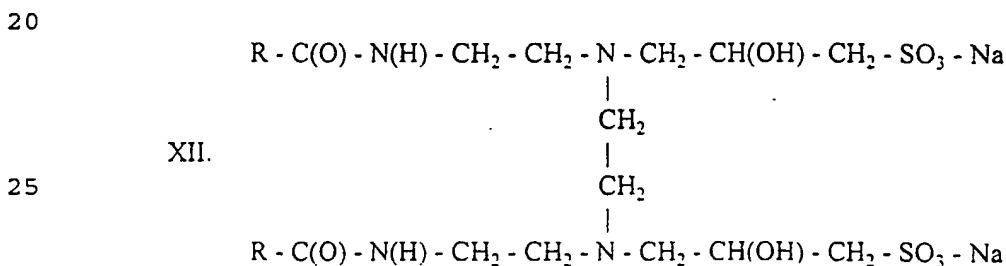
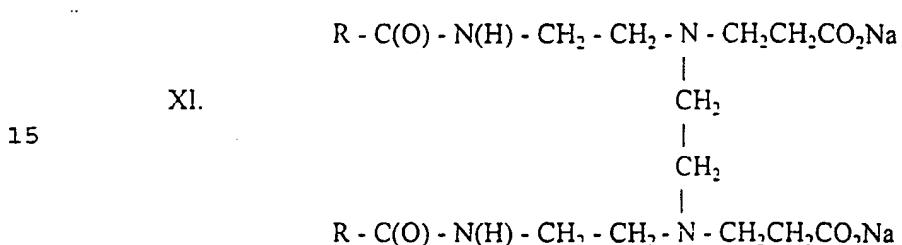
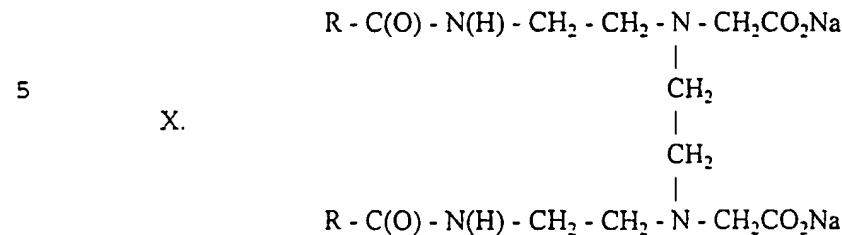
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IX.



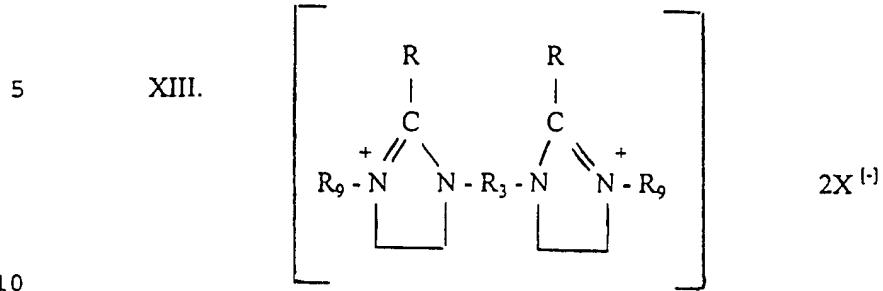
wherein R, R_2 , R_5 , Z, and n are as defined hereinbefore: and m independently equals a number between about 2 and about 10.

Representative compounds of Formula VII include:



30 While the compounds of Formulae VII - XII can be prepared by a variety of synthetic routes, it has been found that they can be produced particularly effectively by a process which utilizes a polyamine reactant having at least four amino groups of which two are terminal primary amines such as triethylene tetramine. These processes are more fully set forth in copending application "Amphoteric Surfactants Having 35 Multiple Hydrophobic and Hydrophilic Groups". U.S.S.N. 08/292,993 filed 08/19/94. the entire disclosure of which is incorporated herein by reference.

Another group of gemini surfactants which have been found to provide the low concentration emulsions of this invention are the cyclic cationic quaternary surfactants of the formula:



wherein R and R₃ are as identified hereinbefore in formula VII: R₉ is independently a C₁ - C₁₀ alkyl or alkylaryl; and X represents a counterion such as an anion illustrated by halogen (Cl, Br, and I), alkylsulfate such as methyl or ethylsulfate, alkylphosphate such as methylphosphate, and the like.

15 Preferably, the compounds used in the present invention comprise those of
Formula XIII in which R_3 is a C_2 - C_4 alkyl, most preferably ethyl, R_9 is a lower alkyl
of from 1 to about 4 carbon atoms, most preferably methyl; and X is halogen or
methylsulfate.

The compounds of Formula XIII can be prepared by a variety of synthetic routes though it has been found that they can be produced particularly effectively by quaternizing a bisimidazoline prepared by a process disclosed and claimed in copending application "Amphoteric Surfactants having Multiple Hydrophobic and Hydrophilic Groups", U.S.S.N. 08/292,993 filed 08/19/94 wherein a polyamine reactant having at least four amino groups, of which two are terminal primary amine groups, is reacted with an acylating agent such as a carboxylic acid, ester, and the naturally occurring triglyceride esters thereof or acid chlorides thereof in an amount

sufficient to provide at least about 1.8 fatty acid groups [R₁C(O)-] per polyamine to provide the bisimidazoline.

Also included in the gemini surfactants useful in this invention are those of the formula:



10 wherein R₁₃ is a sugar moiety, e.g., a monosaccharide, desaccharide, or polysaccharide such as glucose; or a polyhydroxy compound such as glycerol; p is independently 0 to 4; R₃ is as defined above in formula VII; and R₁₄ is a C₁-C₂₂ alkyl or -C(O)R₄ wherein R₄ is as described above.

Some of the compounds such as those described above are set forth more fully
 15 in U.S. Patent 5,534,197 which description is incorporated herein by reference.

In the compounds used in the invention, many of the moieties can be derived from natural sources which will generally contain mixtures of different saturated and unsaturated carbon chain lengths. The natural sources can be illustrated by coconut oil or similar natural oil sources such as palm kernel oil, palm oil, osya oil, rapeseed oil.
 20 castor oil or animal fat sources such as herring oil and beef tallow. Generally, the fatty acids from natural sources in the form of the fatty acid or the triglyceride oil can be a mixture of alkyl radicals containing from about 5 to about 22 carbon atoms.

Illustrative of the natural fatty acids are caprylic (C₈), capric (C₁₀), lauric (C₁₂), myristic (C₁₄), palmitic (C₁₆), stearic (C₁₈), oleic (C₁₈, monounsaturated), linoleic (C₁₈, diunsaturated), linolenic (C₁₈, triunsaturated), ricinoleic (C₁₈, monounsaturated) arachidic (C₂₀), gadolic (C₂₀, monounsaturated), behenic (C₂₂) and erucic (C₂₂). These

fatty acids can be used per se, as concentrated cuts or as fractionations of natural source acids. The fatty acids with even numbered carbon chain lengths are given as illustrative though the odd numbered fatty acids can also be used. In addition, single carboxylic acids, e.g., lauric acid, or other cuts, as suited for the particular application,

5 may be used.

Where desired, the surfactants used in the present invention can be oxyalkylated by reacting the product with an alkylene oxide according to known methods, preferably in the presence of an alkaline catalyst. The free hydroxyl groups of the alkoxylated derivative can then be sulfated, phosphated or acylated using normal 10 methods such as sulfation with sulfamic acid or sulfur trioxide-pyridine complex, or acylation with an acylating agent such as a carboxylic acid, ester, and the naturally occurring triglyceride esters thereof.

For alkylation conditions and commonly used alkylating agents, see Amphoteric Surfactants Vol. 12, Ed. B. R. Bluestein and C. L. Hilton, Surfactant 15 Science Series 1982, pg. 17 and references cited therein, the disclosures of which are incorporated herein by reference.

For sulfation and phosphation, see Surfactant Science Series, Vol. 7, Part 1, S. Shore & D. Berger, page 135, the disclosure of which is incorporated herein by reference. For phosphating review, see Surfactant Science Series, Vol. 7, Part II, E. 20 Jungermann & H. Silbertman, page 495, the disclosure of which is incorporated herein by reference.

The surfactant compositions of the invention are extremely effective in aqueous solution at low concentrations as defined herein. The surfactants of the invention can

be used in any amount needed for a particular application which can be easily determined by a skilled artisan without undue experimentation.

While the gemini surfactants of the invention can be used alone, it has been unexpectedly found that blends of the compounds of the invention with certain other 5 conventional well known anionic, nonionic, cationic and amphoteric surfactants provide synergistic effects in relation to critical micelle concentration (cmc) and surface tension reducing ability, and hence improved detergency.

A. Nonionic Surfactants

10 Nonionic surfactants, including those having an HLB of from 5 to 17, are well known in the detergency art. Examples of such surfactants are listed in U.S. Patent No. 3,717,630, Booth, issued February 20, 1973, and U. S. Patent No. 3,332,880, Kessler et al., issued July 25, 1967, each of which is incorporated herein by reference. Nonlimiting examples of suitable nonionic surfactants which may be used in the 15 present invention are as follows:

(1) The polyethylene oxide condensates of alkyl phenols. These compounds include the condensation products of alkyl phenols having an alkyl group containing from about 6 to 12 carbon atoms in either a straight chain or branched chain configuration with ethylene oxide, said ethylene oxide being present in an amount equal to 5 to 25 moles of ethylene oxide per mole of alkyl phenol. The alkyl substituent in such compounds can be derived, for example, from polymerized propylene, diisobutylene, and the like. Examples of compounds of this type include nonyl phenol condensed with about 9.5 moles of ethylene oxide per mole of nonyl phenol; dodecylphenol condensed with

about 12 moles of ethylene oxide per mole of phenol; dinonyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol; and diisooctyl phenol condensed with about 15 moles of ethylene oxide per mole of phenol. Commercially available nonionic surfactants of this type include Igepal CO-630, marketed by Rhone-Poulenc Inc. and Triton X-45, X-114, X-100, and X-102, all marketed by Union Carbide.

- (2) The condensation products of aliphatic alcohols with from about 1 to about 25 moles of ethylene oxide. The alkyl chain of the aliphatic alcohol can either be straight or branched, primary or secondary, and generally contains from about 8 to about 22 carbon atoms. Examples of such ethoxylated alcohols include the condensation product of myristyl alcohol condensed with about 10 moles of ethylene oxide per mole of alcohol; and the condensation product of about 9 moles of ethylene oxide with coconut alcohol (a mixture of fatty alcohols with alkyl chains varying in length from 10 to 14 carbon atoms). Examples of commercially available nonionic surfactants in this type include Tergitol 15-S-9, marketed by Union Carbide Corporation. Neodol 45-9, Neodol 23-6.5, Neodol 45-7, and Neodol 45-4, marketed by Shell Chemical Company.
- (3) The condensation products of ethylene oxide with a hydrophobic base formed by the condensation of propylene oxide with propylene glycol. The hydrophobic portion of these compounds typically has a molecular weight of from about 1500 to 1800 and exhibits water insolubility. The addition of polyoxyethylene moieties to this hydrophobic portion tends to increase the water solubility of the molecule as a whole, and the liquid character of the product is retained up to the point where the polyoxyethylene content is about

50% of the total weight of the condensation product, which corresponds to condensation with up to about 40 moles of ethylene oxide. Examples of compounds of this type include certain of the commercially available Pluronic surfactants, marketed by Wyandotte Chemical Corporation.

- (4) The condensation products of ethylene oxide with the product resulting from the reaction of propylene oxide and ethylenediamine. The hydrophobic moiety of these products consists of the reaction product of ethylenediamine and excess propylene oxide, said moiety having a molecular weight of from about 2500 to about 3000. This hydrophobic moiety is condensed with ethylene oxide to the extent that the condensation product contains from about 40% to about 80% by weight of polyoxyethylene and has a molecular weight of from about 5,000 to about 11,000. Examples of this type of nonionic surfactant include certain of the commercially available Tetronic compounds, marketed by Wyandotte Chemical Corporation.
- (5) Semi-polar nonionic detergent surfactants include water-soluble amine oxides containing one alkyl moiety of from about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from 1 to about 3 carbon atoms; water-soluble phosphine oxides containing one alkyl moiety of about 10 to 18 carbon atoms and 2 moieties selected from the group consisting of alkyl groups and hydroxyalkyl groups containing from about 1 to 3 carbon atoms; and water-soluble sulfoxides containing one alkyl moiety of from about 10 to 18 carbon atoms and a moiety selected from the group consisting of alkyl and hydroxyalkyl moieties of from about 1 to 3 carbon atoms.

Preferred semi-polar nonionic detergent surfactants are the amine oxide detergent surfactants having the formula:



wherein R^1 is an alkyl, hydroxy alkyl, or alkyl phenyl group or mixtures thereof containing from about 8 to about 22 carbon atoms. R^2 is an alkylene or hydroxy alkylene group containing from 2 to 3 carbon atoms or mixtures thereof, x is from 0 to about 3 and each R^3 is an alkyl or hydroxy alkyl group containing from 1 to about 3 10 carbon atoms or a polyethylene oxide group containing from one to about 3 ethylene oxide groups and said R^3 groups can be attached to each other, e.g., through an oxygen or nitrogen atom to form a ring structure.

Preferred amine oxide detergent surfactants are $C_{10}-C_{18}$ alkyl dimethyl amine oxide, C_8-C_{18} alkyl dihydroxy ethyl amine oxide, and C_{8-12} alkoxy ethyl dihydroxy 15 ethyl amine oxide.

Nonionic detergent surfactants (1)-(4) are conventional ethoxylated nonionic detergent surfactants and mixtures thereof can be used.

Preferred alcohol ethoxylate nonionic surfactants for use in the compositions of the liquid, powder, and gel applications are biodegradable and have the formula



wherein R is a primary or secondary alkyl chain of from about 8 to about 22, preferably from about 10 to about 20 carbon atoms and n is an average of from about 2 to about 12, particularly from about 2 to about 9. The nonionics have an HLB (hydrophilic-lipophilic balance) of from about 5 to about 17, preferably from about 6

about 15. HLB is defined in detail in *Nonionic Surfactants*, by M. J. Schick, Marcel Dekker, Inc., 1966, pages 606-613, incorporated herein by reference. In preferred nonionic surfactants, n is from 3 to 7. Primary linear alcohol ethoxylates (e.g., alcohol ethoxylates produced from organic alcohols which contain about 20% 2-methyl 5 branched isomers, commercially available from Shell Chemical Company under the trademark Neodol) are preferred from a performance standpoint.

Particularly preferred nonionic surfactants for use in liquid, powder, and gel applications include the condensation product of C₁₀ alcohol with 3 moles of ethylene oxide; the condensation product of tallow alcohol with 9 moles of ethylene oxide; the 10 condensation product of coconut alcohol with 5 moles of ethylene oxide; the condensation product of coconut alcohol with 6 moles of ethylene oxide; the condensation product of C₁₂ alcohol with 5 moles of ethylene oxide; the condensation product of C₁₂₋₁₃ alcohol with 6.5 moles of ethylene oxide, and the same condensation product which is stripped so as to remove substantially all lower ethoxylate and 15 nonethoxylated fractions; the condensation product of C₁₂₋₁₃ alcohol with 2.3 moles of ethylene oxide, and the same condensation product which is stripped so as to remove substantially all lower ethoxylated and nonethoxylated fractions; the condensation product of C₁₂₋₁₃ alcohol with 9 moles of ethylene oxide; the condensation product of C₁₄₋₁₅ alcohol with 2.25 moles of ethylene oxide; the condensation product of C₁₄₋₁₅ 20 alcohol with 4 moles of ethylene oxide; the condensation product of C₁₄₋₁₅ alcohol with 7 moles of ethylene oxide; and the condensation product of C₁₄₋₁₅ alcohol with 9 moles of ethylene oxide. For bar soap applications, nonionic surfactants are preferably solids at room temperature with a melting point above about 25° C., preferably above about 30° C. Bar compositions of the present invention made with lower melting nonionic

surfactants are generally too soft, not meeting the bar firmness requirements of the present invention.

Also, as the level of nonionic surfactant increases, i.e., above about 20% by weight of the surfactant, the bar can generally become oily.

5 Examples of nonionic surfactants usable herein, but not limited to bar applications, include fatty acid glycerine and polyglycerine esters, sorbitan sucrose fatty acid esters, polyoxyethylene alkyl and alkyl allyl ethers, polyoxyethylene lanolin alcohol, glycerine and polyoxyethylene glycerine fatty acid esters, polyoxyethylene propylene glycol and sorbitol fatty acid esters, polyoxyethylene lanolin, castor oil or 10 hardened castor oil derivatives, polyoxyethylene fatty acid amides, polyoxyethylene alkyl amines, alkylpyrrolidone, glucamides, alkylpolyglucosides, and mono- and dialkanol amides.

Typical fatty acid glycerine and polyglycerine esters, as well as typical sorbitan sucrose fatty acid esters, fatty acid amides, and polyethylene oxide/polypropylene 15 oxide block copolymers are disclosed by U.S. Patent No. 5,510,042, Hartman et al. incorporated herein by reference.

The castor oil derivatives are typically ethoxylated castor oil. It is noted that other ethoxylated natural fats, oils or waxes are also suitable.

Polyoxyethylene fatty acid amides are made by ethoxylation of fatty acid 20 amides with one or two moles of ethylene oxide or by condensing mono- or diethanol amines with fatty acid.

Polyoxyethylene alkyl amines include those of formula: $\text{RNH}-(\text{CH}_2\text{CH}_2\text{O})_n\text{H}$, wherein R is C_6 to C_{22} alkyl and n is from 1 to about 100.

Monoalkanol amides include those of formula: $\text{RCO}(\text{NH})\text{R}'\text{OH}$, wherein R is $\text{C}_6\text{-C}_{22}$ alkyl and R' is C_1 to C_6 alkylene. Dialkanol amides are typically mixtures of:

diethanolamide: $\text{RCO}(\text{NH})(\text{CH}_2\text{CH}_2\text{OH})_2$;

amide ester: $\text{RCO}(\text{NH})(\text{CH}_2\text{CH}_2\text{OH})-\text{CH}_2\text{CH}_2\text{OOCR}$;

amine ester: $\text{RCOOCH}_2\text{CH}_2\text{NHCH}_2\text{CH}_2\text{OH}$; and

amine soap: $\text{RCOOH}_2\text{N}(\text{CH}_2\text{CH}_2\text{OH})_2$,

wherein R in the above formulas is an alkyl of from 6 to 22 carbon atoms.

Examples of preferred but not limiting surfactants for detergent bar products are the following:

10 Straight-Chain Primary Alcohol Alkoxylates

The deca-, undeca-, dodeca-, tetradeca-, and pentadeca-ethoxylates of n-hexadecanol, and n-hexadecanol, and n-octadecanol having an HLB within the range recited herein are useful nonionics in the context of this invention. Exemplary ethoxylated primary alcohols useful herein as the conventional nonionic surfactants of the compositions are n-C₁₈EO(10); n-C₁₄EO(13); and n-C₁₀EO(11). The ethoxylates of mixed natural or synthetic alcohols in the "tallow" chain length range are also useful herein. Specific examples of such materials include tallow-alcohol-EO(11), tallow-alcohol-EO(18), and tallow-alcohol-EO(25).

Straight-Chain Secondary Alcohol Alkoxylates

20 The deca-, undeca-, dodeca-, tetradeca-, pentadeca-, octadeca-, and nonadeca-
ethoxylates of 3-hexadecanol, 2-octadecanol, 4-eicosanol, and 5-eicosanol having an
HLB within the range recited herein are useful conventional nonionics in the context of
this invention. Exemplary ethoxylated secondary alcohols useful herein are 2-
 C_{16} EO(11); 2- C_{20} EO(11); and 2- C_{16} EO(14).

Alkyl Phenol Alkoxylates

As in the case of the alcohol alkoxylates, the hexa- through octadeca-ethoxylates of alkylated phenols, particularly monohydric alkylphenols, having an HLB within the range recited herein are useful as conventional nonionic surfactants in the instant compositions. The hexa- through octadeca-ethoxylates of p-tridecylphenol, m-pentadecylphenol, and the like, are useful herein. Exemplary ethoxylated alkylphenols useful in the mixtures herein are: p-tridecylphenol EO(11) and p-pentadecylphenol EO(18). Especially preferred is Nonyl Nonoxynol-49 known as Igepal[®] DM-880 from Rhone-Poulenc Inc.

10. As used herein and as generally recognized in the art, a phenylene group in the nonionic formula is the equivalent of an alkylene group containing from 2 to 4 carbon atoms. For present purposes, nonionics containing a phenylene group are considered to contain an equivalent number of carbon atoms calculated as the sum of the carbon atoms in the alkyl group plus about 3.3 carbon atoms for each phenylene group.

15 Olefinic Alkoxylates

The alkenyl alcohols, both primary and secondary, and alkenyl phenols corresponding to those disclosed immediately hereinabove can be ethoxylated to an HLB within the range recited herein and used as the conventional nonionic surfactants of the instant compositions.

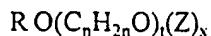
20 Branched Chain Alkoxylates

Branched chain primary and secondary alcohols which are available can be ethoxylated and employed as conventional nonionic surfactants in compositions herein.

The above ethoxylated nonionic surfactants are useful in the present compositions alone or in combination, and the term "nonionic surfactant" encompasses mixed nonionic surface active agents.

Alkylpolysaccharides

5 Still further suitable nonionic surfactants of this invention include alkylpolysaccharides, preferably alkylpolyglucosides of the formula:



wherein

Z is derived from glucose;

10 R is a hydrophobic group selected from the group consisting of a C₁₀-C₁₈, preferably a C₁₂-C₁₄, alkyl group, alkyl phenyl group, hydroxyalkyl group, hydroxyalkylphenyl group, and mixtures thereof;

n is 2 or 3; preferably 2;

t is from 0 to 10; preferably 0; and

15 x is from 1.5 to 8; preferably 1.5 to 4; more preferably from 1.6 to 2.7.

These surfactants are disclosed in U.S. Patent Nos. 4,565,647, Llenado, issued January 21, 1986; 4,536,318, Cook et al., issued August 20, 1985; 4,536,317, Llenado et al., issued August 20, 1985; 4,599,188 Llenado, issued July 8, 1986; and 4,536,319, Payne, issued August 20, 1985; all of which are incorporated herein by reference.

20 The compositions of the present invention can also comprise mixtures of the above nonionic surfactants.

A thorough discussion of nonionic surfactants for detergent bar and liquid products is presented by U.S. Patent Nos. 5,510,042, Hartman et al., and 4,483,779, Llenado, et al., incorporated herein by reference.

B. Anionic Surfactants

Anionic surfactants include any of the known hydrophobes attached to a carboxylate, sulfonate, sulfate or phosphate polar, solubilizing group including salts. Salts may be the sodium, potassium, ammonium and amine salts of such surfactants.

5 Useful anionic surfactants can be organic sulfuric reaction products having in their molecular structure an alkyl group containing from about 8 to about 22 carbon atoms and a sulfonic acid or sulfuric acid ester group, or mixtures thereof. (Included in the term "alkyl" is the alkyl portion of acyl groups.) Examples of this group of synthetic detergents surfactants which can be used in the present invention are the alkyl sulfates.

10 especially those obtained by sulfating the higher alcohols (C_8 - C_{18} carbon atoms) produced from the glycerides of tallow or coconut oil; and alkyl benzene sulfonates.

Other useful anionic surfactants herein include the esters of alpha-sulfonated fatty acids preferably containing from about 6 to 20 carbon atoms in the ester group; 2-acyloxyalkane-1-sulfonic acids preferably containing from about 2 to 9 carbon atoms 15 in the acyl group and from about 9 to about 23 carbon atoms in the alkane moiety; alkyl ether sulfates preferably containing from about 10 to 20 carbon atoms in the alkyl group and from about 1 to 30 moles of ethylene oxide; olefin sulfonates preferably containing from about 12 to 24 carbon atoms; and beta-alkyloxy alkane sulfonates 20 preferably containing from about 1 to 3 carbon atoms in the alkyl group and from about 8 to 20 carbon atoms in the alkane moiety.

Anionic surfactants based on the higher fatty acids, i.e., "soaps" are useful anionic surfactants herein. Higher fatty acids containing from about 8 to about 24 carbon atoms and preferably from about 10 to about 20 carbon atoms and the coconut and tallow soaps can also be used herein as corrosion inhibitors.

Preferred water-soluble anionic organic surfactants herein include linear alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; branched alkyl benzene sulfonates containing from about 10 to about 18 carbon atoms in the alkyl group; the tallow range alkyl sulfates; the coconut range alkyl glyceryl sulfonates; alkyl ether (ethoxylated) sulfates wherein the alkyl moiety contains from about 12 to 18 carbon atoms and wherein the average degree of ethoxylation varies between 1 and 12, especially 3 to 9; the sulfated condensation products of tallow alcohol with from about 3 to 12, especially 6 to 9, moles of ethylene oxide; and olefin sulfonates containing from about 14 to 16 carbon atoms.

10 Specific preferred anionics for use herein include: the linear C₁₀-C₁₄ alkyl benzene sulfonates (LAS); the branched C₁₀-C₁₄ alkyl benzene sulfonates (ABS); the tallow alkyl sulfates, the coconut alkyl glyceryl ether sulfonates; the sulfated condensation products of mixed C₁₀-C₁₈ tallow alcohols with from about 1 to about 14 moles of ethylene oxide; and the mixtures of higher fatty acids containing from 10 to 15 18 carbon atoms.

It is to be recognized that any of the foregoing anionic surfactants can be used separately herein or as mixtures. Moreover, commercial grades of the surfactants can contain non-interfering components which are processing by-products. For example, commercial alkaryl sulfonates, preferably C₁₀-C₁₄, can comprise alkyl benzene sulfonates, alkyl toluene sulfonates, alkyl naphthalene sulfonates and alkyl polycatenoid sulfonates. Such materials and mixtures thereof are fully contemplated for use herein.

Other examples of the anionic surfactants used herein include fatty acid soaps, ether carboxylic acids and salts thereof, alkane sulfonate salts, α -olefin sulfonate salts.

sulfonate salts of higher fatty acid esters, higher alcohol sulfate ester or ether ester salts, alkyl, preferably higher alcohol phosphate ester and ether ester salts, and condensates of higher fatty acids and amino acids.

Fatty acid soaps include those having the formula: R-C(O)OM, wherein R is C₆ to C₂₂ alkyl and M is preferably sodium.

Salts of ether carboxylic acids and salts thereof include those having the formula: R-(OR¹)_n-OCH₂C(O)OM, wherein R is C₆ to C₂₂ alkyl, R¹ is C₂ to C₁₀, preferably C₂ alkyl, and M is preferably sodium.

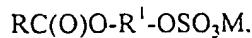
Alkane sulfonate salts and *α*-olefin sulfonate salts have the formula: R-SO₃M, wherein R is C₆ to C₂₂ alkyl or *α*-olefin, respectively, and M is preferably sodium.

Sulfonate salts of higher fatty acid esters include those having the formula:



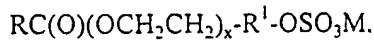
wherein R is C₁₂ to C₂₂ alkyl, R¹ is C₁ to C₁₈ alkyl and M is preferably sodium.

Higher alcohol sulfate ester salts include those having the formula:



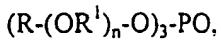
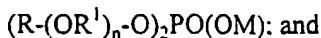
wherein R is C₁₂-C₂₂ alkyl, R¹ is C₁-C₁₈ hydroxyalkyl, M is preferably sodium.

Higher alcohol sulfate ether ester salts include those having the formula:



wherein R is C₁₂-C₂₂ alkyl, R¹ is C₁-C₁₈ hydroxyalkyl, M is preferably sodium and x is an integer from 5 to 25.

Higher alcohol phosphate ester and ether ester salts include compounds of the formulas:



wherein R is alkyl or hydroxyalkyl of 12 to 22 carbon atoms. R¹ is C₂H₄, n is an 5 integer from 5 to 25, and M is preferably sodium.

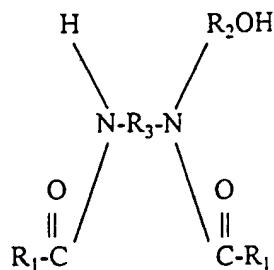
Other anionic surfactants herein are sodium coconut oil fatty acid monoglyceride sulfonates and sulfates; sodium or potassium salts of alkyl phenol ethylene oxide ether sulfates containing from about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl groups contain from about 8 to about 12 10 carbon atoms; and sodium or potassium salts of alkyl ethylene oxide ether sulfates containing about 1 to about 10 units of ethylene oxide per molecule and wherein the alkyl group contains from about 10 to about 20 carbon atoms.

C. Cationic Surfactants

Preferred cationic surfactants of the present invention are the reaction products 15 of higher fatty acids with a polyamine selected from the group consisting of hydroxyalkylalkylenediamines and dialkylenetriamines and mixtures thereof.

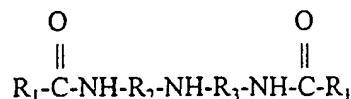
A preferred component is a nitrogenous compound selected from the group consisting of:

(i) the reaction product mixtures of higher fatty acids with hydroxyalkylalkylenediamines in a molecular ratio of about 2:1, said reaction product containing a composition having a compound of the formula:



wherein R_1 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{21}$ hydrocarbon group and R_2 and R_3 are divalent $\text{C}_1\text{-C}_3$ alkylene groups; commercially available as Mazamide 6 from PPG;

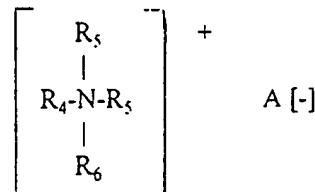
- (ii) the reaction product of higher fatty acids with dialkylenetriamines in a molecular ratio of about 2:1; said reaction product containing a composition having a compound of the formula:



wherein R_1 , R_2 and R_3 are as defined above; and mixtures thereof.

Another preferred component is a cationic nitrogenous salt containing one long chain acyclic aliphatic $\text{C}_{15}\text{-C}_{22}$ hydrocarbon group selected from the group consisting of:

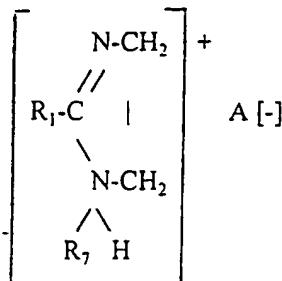
- (i) acyclic quaternary ammonium salts having the formula:



wherein R_4 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{22}$ hydrocarbon group. R_5 and R_6 are $\text{C}_1\text{-C}_4$ saturated alkyl or hydroxyalkyl groups. and $\text{A} [-]$ is an anion. especially as described in more detail hereinafter. examples of these

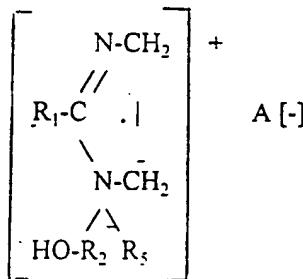
surfactants are sold by Witco Chemical Company under the Adogen trademarks;

(ii) substituted imidazolinium salts having the formula:



wherein R_1 is an acyclic aliphatic $\text{C}_{15}\text{-C}_{21}$ hydrocarbon group, R_7 is a hydrogen or a $\text{C}_1\text{-C}_4$ saturated alkyl or hydroxyalkyl group, and $\text{A} [-]$ is an anion

(iii) substituted imidazolinium salts having the formula:



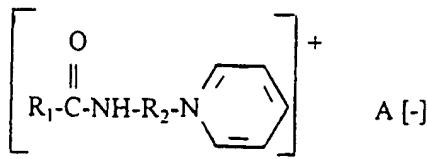
wherein R_2 is a $\text{C}_1\text{-C}_3$ alkyl group and R_1 , R_5 and $\text{A} [-]$ are as defined above; an example of which is commercially available under the Monaquat ISIES trademark from Mona Industries, Inc.;

(iv) alkylpyridinium salts having the formula:



wherein R_4 is an acyclic aliphatic $\text{C}_{16}\text{-C}_{22}$ hydrocarbon group and $\text{A} [-]$ is an anion; and

(v) alkanamide alkylene pyridinium salts having the formula:

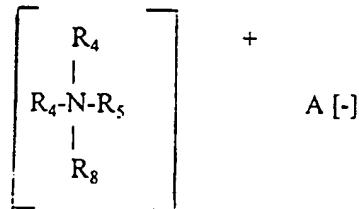


wherein R_1 is an acyclic aliphatic $\text{C}_{15}\text{-}\text{C}_{21}$ hydrocarbon group, R_2 is a divalent $\text{C}_1\text{-}\text{C}_3$ alkylene group, and $\text{A} [-]$ is an ion group; and mixtures thereof.

Another class of preferred cationic nitrogenous salts having two or more long chain acyclic aliphatic $\text{C}_{15}\text{-}\text{C}_{22}$ hydrocarbon groups or one said group and an arylalkyl group are selected from the group consisting of:

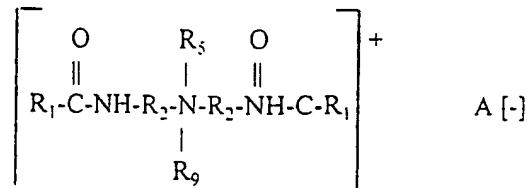
5

(i) acyclic quaternary ammonium salts having the formula:



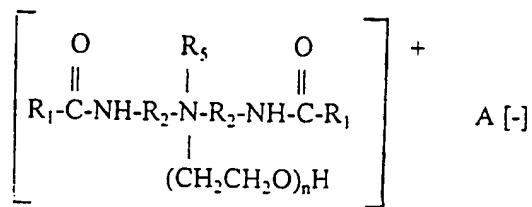
wherein each R_4 is an acyclic aliphatic $\text{C}_{15}\text{-}\text{C}_{22}$ hydrocarbon group, R_5 is a $\text{C}_1\text{-}\text{C}_4$ saturated alkyl or hydroxyalkyl group, R_8 is selected from the group consisting of R_4 and R_5 groups, and $\text{A} [-]$ is an anion defined as above; examples of which are commercially available from Witco Company under the Adogen trademarks;

(ii) diamido quaternary ammonium salts having the formula:



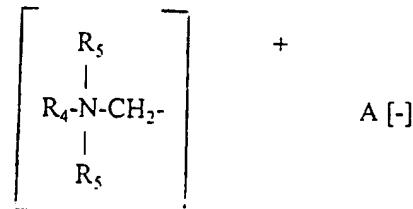
wherein each R_1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group, R_2 is a divalent alkylene group having 1 to 3 carbon atoms, R_5 and R_9 are C_1 - C_4 saturated alkyl or hydroxyalkyl groups, and $A [-]$ is an anion; examples of which are sold by Witco Chemical Company under the Varisoft trademark;

(iii) diamino alkoxylated quaternary ammonium salts having the formula:



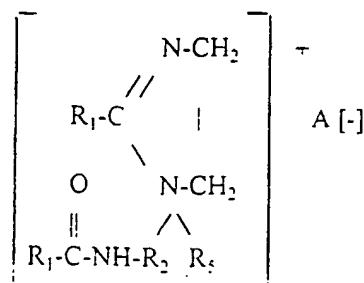
wherein n is equal to 1 to about 5, and R_1 , R_2 , R_5 and $A [-]$ are as defined above;

(iv) quaternary ammonium compounds having the formula:



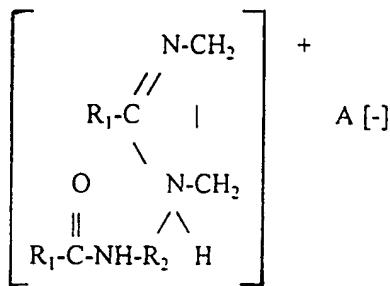
wherein each R_4 is an acyclic aliphatic C_{15} - C_{22} hydrocarbon group, each R_5 is a C_1 - C_4 saturated alkyl or hydroxyalkyl group, and $A [-]$ is an anion; examples of such surfactants are available from Stepan Chemical Company under the Ammonyx[®] 490 trademark;

(v) substituted imidazolinium salts having the formula:



wherein each R_1 is an acyclic aliphatic C_{15} - C_{21} hydrocarbon group, R_2 is a divalent alkylene group having 1 to 3 carbon atoms, and R_5 and A [-] are as defined above; examples are commercially available from Witco Chemical Company under the Varisoft 475 and Varisoft 445 trademarks; and

(vi) substituted imidazolinium salts having the formula:



wherein R_1 , R_2 and A - are as defined above; and mixtures thereof.

The more preferred cationic conventional surfactant is selected from the group consisting of an alkyltrimethylammonium salt, a dialkyldimethylammonium salt, an alkylidimethylbenzylammonium salt, an alkylpyridinium salt, an alkylisoquinolinium salt, benzethonium chloride, and an acylamino acid cationic surfactant.

5 Anion A

In the cationic nitrogenous salts herein, the anion A [-] provides electrical neutrality. Most often, the anion used to provide electrical neutrality in these salts is a halide, such as chloride, bromide, or iodide. However, other anions can be used, such as methylsulfate, ethylsulfate, acetate, formate, sulfate, carbonate, and the like.

10 Chloride and methylsulfate are preferred herein as anion A.

Cationic surfactants are commonly employed as fabric softeners in compositions added during the rinse cycle of clothes washing. Many different types of fabric conditioning agents have been used in rinse cycle added fabric conditioning

compositions as disclosed by U.S. Patent No. 5,236,615, Trinh et al. and U.S. Patent No. 5,405,542, Trinh et al., both patents herein incorporated by reference in their entirety. The most favored type of agent has been the quaternary ammonium compounds. Many such quaternary ammonium compounds are disclosed for example. 5 by U.S. Patent No. 5,510,042, Hartman et al. incorporated herein by reference in its entirety. These compounds may take the form of noncyclic quaternary ammonium salts having preferably two long chain alkyl groups attached to the nitrogen atoms. Additionally, imidazolinium salts have been used by themselves or in combination with other agents in the treatment of fabrics as disclosed by U.S. Patent No. 4,127,489. 10 Pracht, et al., incorporated herein by reference in its entirety. U.S. Patent No. 2,874,074, Johnson discloses using imidazolinium salts to condition fabrics; and U.S. Patent No. 3,681,241, Rudy, and U.S. Patent No. 3,033,704, Sherrill et al. disclose fabric conditioning compositions containing mixtures of imidazolinium salts and other fabric conditioning agents. These patents are incorporated herein by reference in their 15 entirety.

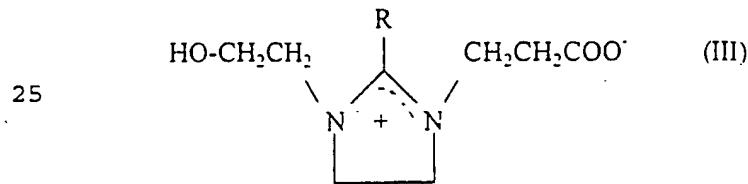
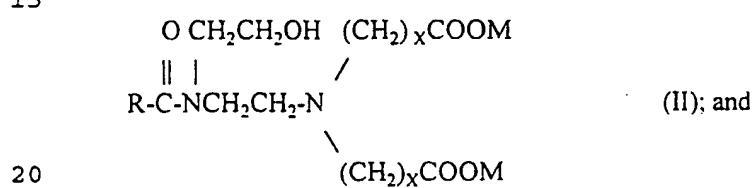
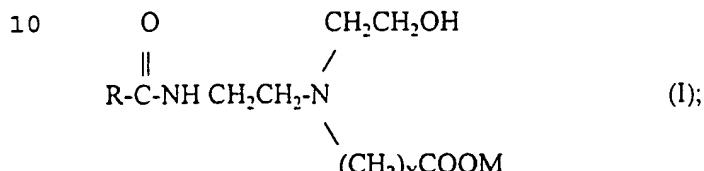
D. Amphoteric Surfactants

Amphoteric surfactants have a positive or negative charge or both on the hydrophilic part of the molecule in acidic or alkaline media.

Examples of the amphoteric surfactants which can be used herein include 20 amino acid, betaine, sultaine, phosphobetaines, imidazolinium derivatives, soybean phospholipids, and yolk lecithin. Examples of suitable amphoteric surfactants include the alkali metal, alkaline earth metal, ammonium or substituted ammonium salts of alkyl amphocarboxyglycinates and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycinates and alkyl

amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Other suitable amphoteric surfactants include alkyliminopropionates, alkyl iminodipropionates and alkyl amphopropylsulfonates having between 12 and 18 carbon atoms, alkylbetaines and amidopropylbetaines and alkylsultaines and 5 alkylamidopropylhydroxy sultaines wherein alkyl represents an alkyl group having 6 to 20 carbon atoms are especially preferred.

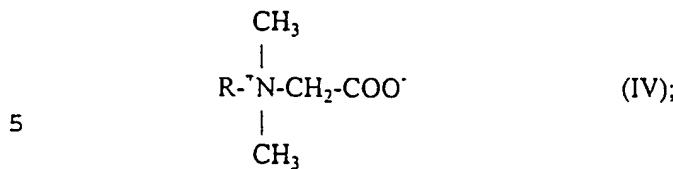
Particularly useful amphoteric surfactants include both mono and dicarboxylates such as those of the formulae:



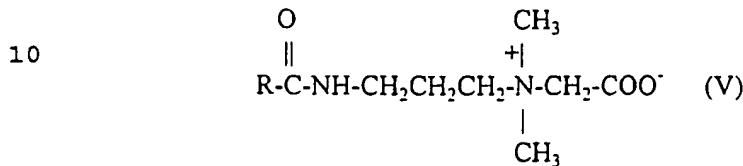
30 wherein R is an alkyl group of 6-20 carbon atoms. x is 1 or 2 and M is hydrogen or sodium. Mixtures of the above structures are particularly preferred.

Other formulae for the above amphoteric surfactants include the following:

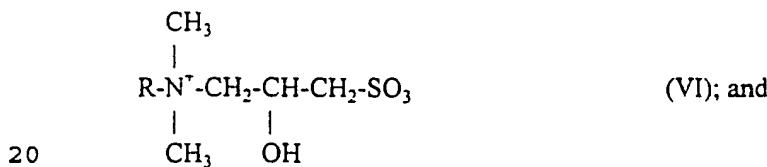
Alkyl betaines



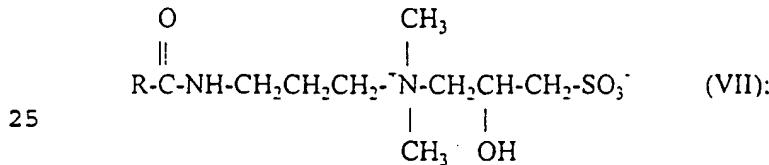
Amidopropyl betaines



15 Alkyl sultaines



Alkyl amidopropylhydroxy sultaines



where R is an alkyl group of 6-20 carbon atoms and M is hydrogen or sodium.

Of the above amphoteric surfactants, particularly preferred are the alkali salts of alkyl amphocarboxyglycinates and alkyl amphocarboxypropionates, alkyl amphodipropionates, alkyl amphodiacetates, alkyl amphoglycinates, alkyl amphopropyl sulfonates and alkyl amphopropionates wherein alkyl represents an alkyl group having 6 to 20 carbon atoms. Even more preferred are compounds wherein the

alkyl group is derived from coconut oil or is a lauryl group, for example, cocoamphodipropionate. Such cocoamphodipropionate surfactants are commercially sold under the trademarks Miranol C2M-SF CONC. and Miranol FBS by Rhone-Poulenc Inc.

5 Other commercially useful amphoteric surfactants are available from Rhone-Poulenc Inc. and include:

cocoamphoacetate (sold under the trademarks MIRANOL CM CONC. and MIRAPON FA),
cocoamphopropionate (sold under the trademarks MIRANOL CM-SF CONC. and MIRAPON FAS).
cocoamphodiacetate (sold under the trademarks MIRANOL C2M CONC. and MIRAPON FB),
lauroamphoacetate (sold under the trademarks MIRANOL HM CONC. and MIRAPON LA),
lauroamphodiacetate (sold under the trademarks MIRANOL H2M CONC. and MIRAPON LB),
lauroamphodipropionate (sold under the trademarks MIRANOL H2M SF CONC. AND MIRAPON LBS).
lauroamphodiacetate obtained from a mixture of lauric and myristic acids (sold under the trademark MIRANOL BM CONC.), and
cocoamphopropyl sulfonate (sold under the trademark MIRANOL CS CONC.)

Somewhat less preferred are:

caproamphodiacetate (sold under the trademark MIRANOL S2M CONC.),
caproamphoacetate (sold under the trademark MIRANOL SM CONC.).
caproamphodipropionate (sold under the trademark MIRANOL S2M-SF CONC.), and
stearoamphoacetate (sold under the trademark MIRANOL DM).

The aqueous surfactant compositions of the invention comprise a concentration of surfactant equal to or less than the cmc of corresponding conventional surfactants 5 assuming that the gemini is represented in the conventional surfactants as a surfactant having only one hydrophobic grouping and one hydrophilic grouping corresponding to those in the gemini surfactant. Preferably, the total surfactant loading is equal to or less than 80% and more preferably equal to or less than 60% of the cmc of the conventional surfactants in the final use area. In another embodiment, the total aqueous surfactant 10 concentration at end-use level is less than or equal to about 0.01% total surfactant on an active basis, preferably less than about or equal to 0.008%, more preferably from less than about or equal to 0.006%; the lower limit being an emulsifyingly effective amount. The gemini surfactant ranges from 100% to about 10%, preferably from 100% to about 20% and more preferably from 100% to about 35% of the total active surfactant in the 15 end-use compositions. The remainder of the surfactant actives comprise other surfactants not claimed under the term "gemini surfactants" including conventional and other difunctional or polyfunctional surfactants.

Specifically this invention relates to surfactant compositions comprising:

1) from about 10% to about 100% by weight of nonionic, cationic, anionic, or amphoteric gemini surfactants or a combination thereof ; and

2) from about 0% to 90% conventional anionic, nonionic, cationic, or amphoteric, surfactants or mixtures thereof.

5 The anionic, nonionic, cationic, and amphoteric conventional surfactants useful in this invention have been illustrated hereinbefore. Further description of nonionic detergents can be found in U.S. Pat. No. 4,483,780, the entire disclosure of which is incorporated herein by reference. Other ingredients and unsaturated soaps are also disclosed in U.S. Pat. No. 4,483,780.

10 These surfactant systems of the present invention can be manufactured and used in a variety of detergent composition forms such as solids, powders, granules, pastes, and liquids.

15 It has been found that certain combinations of the surfactants of this invention can provide unusually good detergency at very low use levels. Detergent compositions prepared utilizing the instant surfactant compositions can be used in laundering processes by forming dilute aqueous solutions of the detergent compositions containing said surfactant compositions and agitating same with soiled fabrics. The surfactant compositions of the instant invention can be used in detergent compositions at from about 0.5% to about 80%, preferably from about 2% to about 50% by weight.

20 based on the total weight of the detergent composition.

Any of commonly used auxiliary additives. e.g., inorganic salts such as Glauber salt and common salt, builders, humectants, solubilizing agents, UV absorbers, pH adjusting agents, softeners, soil release polymers, soil anti-redeposition agents, conditioning polymers (cationic) for hair and fabric softening, chelating agents, and

viscosity modifiers may be added to the surfactant compositions of the invention to form the detergent compositions as the ultimate end-use aqueous surfactant/composition requires.

Such detergent compositions provide excellent detergency at very low 5 surfactant use concentrations, and can be formulated to provide different sudsing patterns by varying the amounts and types of the gemini surfactants used and the nature of the other anionic and nonionic surfactants present.

The gemini surfactants of the invention are extremely mild and non-irritating to both eyes and skin and exhibit low toxicity; enhanced wetting speed, greater surface 10 tension reduction, low and high foaming profile depending on the gemini used, and foam stabilization properties. They also provide excellent compatibility with other surfactants. The products of the invention are stable over a wide pH range and are biodegradable. These properties make these surfactants adaptable for use in products ranging from cosmetics to industrial applications, such as for non-irritating shampoos, e.g., baby 15 shampoos, body shampoos, bubble baths, bath gels, hair conditioning gels, lotions, skin creams, make up removal creams, detergents, fabric softeners and other washing and cosmetic products that contact the skin. The surfactants of the invention can also find use as hard surface cleaners including cars, dishes, toilets, floors, and the like; laundry detergents and soaps; metal working aids; and the like.

20 This invention will now be described with reference to the following non-limiting examples which are provided for purposes of convenient reference and are illustrative of the procedures by which the compositions of the invention can be prepared.

All percentages, parts and ratios herein are by active weight unless otherwise specified.

EXAMPLE 1

Since emulsifying and detergency power is related to oil-water interfacial tension, equilibrium interfacial tension in dynes/cm between hydrocarbon (heptane) and water is determined by the spinning droplet method on compositions shown in Table 1 at 30°C. The results are reported in Table 1.

Table 1
Equilibrium Interfacial Tension in Dynes/cm

10

Concen- tration of Surfact- ants	Polyoxy- ethylene (13) methylene bis(octyl- phenol)	Polyoxy- ethylene (22) methylene bis(octyl- phenol)	Polyoxy- ethylene (7.5) octylphenol	Polyoxy- ethylene (9.5) octylphenol
0.005%	2.03	3.30	13.0	12.0
0.01%	1.66	3.15	8.39	8.56
0.05%	1.32	2.66	1.22	1.81
0.1%	1.25	2.66	0.92	1.63
0.28%	1.65	3.05	1.68	2.30

It can be seen from Table 1 that interfacial tension of the gemini surfactants of the invention is significantly lower than that of single conventional surfactants at and below 0.01%.

15

EXAMPLE 2

Oil-in-water emulsions are prepared using the following formulation of 10% mineral oil, about 90% water and 0.01% surfactant active (based on water phase).

The coarse emulsions are prepared by vortex mixing each composition for 30 seconds. Each emulsion is characterized by droplet size using an optical microscope, the smaller average droplet size indicating a greater degree of emulsification. Stability is determined by the degree of separation of oil at 23°C respectively, the lower the 5 percent coalescence, the greater the stability. The results are reported in Table 2.

Table 2

	SURFACTANT	AVG. DROPLET SIZE (μm)	AMT. OF OIL COALESCENCE AFTER 2 DAYS
Present Invention	Polyoxyethylene (13) methylene bis(octylphenol)	0.2	0%
Present Invention	Polyoxyethylene (22) methylene bis(octylphenol)	0.3	3%
Control	Polyoxyethylene (7.5) octylphenol	0.7	90%
Control	Polyoxyethylene (9.5) octylphenol	0.8	95%

It can be seen from Table 2 that emulsions prepared with polyoxyethylene 10 methylene bis(octylphenol) gemini surfactants are significantly better than emulsions prepared with the conventional surfactant polyoxyethylene octylphenol.

EXAMPLE 3

The oil-in-water emulsions are prepared using a formulation of 65% mineral oil, about 35% water and 0.028% surfactant active (based on water). 15 The emulsions are prepared by blending in a rotor-stator type mixer (2000 rpm) for 3 min. Emulsions are characterized by droplet size using an optical microscope and

stability by degree of separation of oil at 23°C respectively. The results are reported in Table 3 as follows:

Table 3

	SURFACTANT	AVG. DROPLET SIZE (μm)	AMT. OF OIL COALESCENCE AFTER 10 DAYS
Present Invention	Polyoxyethylene (13) methylene bis(octylphenol)	50	0%
Present Invention	Polyoxyethylene (22) methylene bis(octylphenol)	70	3%
Control	Polyoxyethylene (9.5) octylphenol	100	15%

5 It can be seen from Table 3 that emulsions prepared with polyoxyethylene methylene bisoctylphenol are significantly better than those prepared with the conventional surfactant polyoxyethylene octylphenol.

EXAMPLE 4

10

Amphoteric and cationic gemini surfactants are used as emulsifiers for mineral oil and compared to corresponding conventional surfactants. The results are shown in Table 4.

Table 4

	SURFACTANTS	AMT. OF SURFACTANTS (WT)	AMT. OF OIL COALESCENCE (3 DAYS)
Invention	Disodium biscocoampho acetate (Structure X, R=Coco)	0.05%	5%
Control	Sodium cocoampho acetate	0.05%	10%
Invention	Disodium biscocoampho acetate (Structure X, R=Coco)	0.01%	50%
Control	Sodium cocoampho acetate	0.01%	100%
Invention	Coco bisimidazoline diquat (Structure XIII, R=Coco, R ₉ =CH ₃ , R ₃ =CH ₂ CH ₂ , X=CH ₃ SO ₄ ⁻)	0.8%	0%
Control	Dodecyl trimethyl ammonium bromide	0.8%	5%
Invention	Coco bisimidazoline diquat (Structure XIII, R=Coco, R ₉ =CH ₃ , R ₃ =CH ₂ CH ₂ , X=CH ₃ SO ₄ ⁻)	0.08%	5%
Control	Dodecyl trimethyl ammonium bromide	0.08%	100%

*oil/water = 40/60 (w/w)

5 Systems emulsified with gemini amphoteric and cationic surfactants as disclosed herein are significantly more stable than those prepared using similar amounts of corresponding conventional surfactants.

EXAMPLE 5

The following examples illustrate the compositions and method of the present 10 invention in detergent systems. All percentages, parts and ratios herein are by active weight unless otherwise specified.

Table 5
Composition of Detergents

INGREDIENTS	COMPOSITION 1 (INVENTION)	COMPOSITION 2 (CONTROL)
Polyoxyethylene (13) methylene bis(octylphenol)	7%	---
Polyoxyethylene (7.5) octylphenol	----	7%
Monoethanolamine	2%	2%
Triethanolamine	2%	2%
Water	balance	balance

Detergency for clay soil and dust-sebum on different fabric(s) are evaluated in a

5 Terg-O-Tometer from United States Testing under conditions of 150 ppm hard water, 37.8°C and 12 minute wash cycle. The cleaning effectiveness is measured by the difference in reflectance with the Spectro Gard Color system, from Byk-gardner, before and after washing. Percent reflectance correlates to detersity. Better detersity and cleanliness is evidenced by higher numbers of difference in reflectance.

10 The detersity results are reported at the corresponding surfactant concentration use levels in the final washing solution upon dilution of the compositions in Table 5. The following results (Table 6) show a slight disadvantage for the gemini surfactant over its conventional counterpart surfactant on clay soil using a relatively higher use level. However, the performance is equivalent at 0.01% concentration. and greater effectiveness for the gemini surfactant is observed at amounts below 0.01%.

Table 6

CLAY SOIL UNBUILT SYSTEMS	POLYESTER	COTTON/ POLYESTER	COTTON
Composition 1 - 0.02%	39.5	30.5	17.5
Composition 2 - 0.02%	41.5	34.0	24.5
Composition 1 - 0.01%	38.0	29.5	21.0
Composition 2 - 0.01%	37.5	29.0	20.0
Composition 1 - 0.005%	37.0	32.5	20.0
Composition 2 - 0.005%	35.0	30.5	18.5

Table 7 shows the detergency with dust-sebum. It can be seen that gemini surfactant shows no significant advantage over the traditional surfactants at 0.02% surfactant use concentration, and especially lower performance on polyester fabric. However, gemini surfactants compositions of the invention show a significant advantage over the traditional detergent blend on dust-sebum cotton detergency at 0.01% usage levels, and this trend is more obvious at the even lower level, 0.005%.

10

Table 7

DUST-SEBUM UNBUILT SYSTEMS	POLYESTER	POLYESTER/ COTTON	COTTON
Composition 1 - 0.02%	41.5	40.5	26.5
Composition 2 - 0.02%	46.0	43.0	25.0
Composition 1 - 0.01%	39.0	34.0	21.50
Composition 2 - 0.01%	38.0	34.5	17.5
Composition 1 - 0.005%	34.0	30.5	18.5
Composition 2 - 0.005%	13.0	13.5	13.0

The reflectance data obtained from compositions 1 and 2 at 0.01% and 0.005% is also shown in graph form in Figures 1 and 2.

EXAMPLE 6

Mixed gemini/conventional surfactant systems shows the same trend of low use level, superior performance as illustrated in the following example:

Table 8

INGREDIENT	COMPOSITION 3 (INVENTION)	COMPOSITION 4 (CONTROL)
Sodium dodecylbenzene sulfonate	3.5%	3.5%
Polyoxyethylene (13) methylene bis(octylphenol)	3.5%	-
Polyoxyethylene (7.5) octylphenol	-	3.5%
Monoethanolamine	2%	2%
Triethanolamine	2%	2%
Water	balance	balance

5

The following detergency performance of the compositions of Table 8 is found.

Table 9

DUST-SEBUM UNBUILT SYSTEMS	POLYESTER	POLYESTER/ COTTON	COTTON
Composition 3 - 0.014%	37.5	37	24
Composition 4 - 0.014%	40.5	41	24.5
Composition 3 - 0.005%	26	27	17.5
Composition 4 - 0.005%	18	22	14
Composition 3 - 0.001%	11	12	12
Composition 4 - 0.001%	0	7.5	10

10

The reflectance data obtained from compositions 3 and 4 at 0.005% and 0.001% is also shown in graph form in Figures 3 and 4.

Very low use concentrations in a mixed surfactant system with gemini nonionic surfactant excels over conventional nonionic surfactant systems. Performance differences become more exaggerated at very low use concentrations.

5

EXAMPLE 7

The gemini surfactant can be also blended with conventional anionic and nonionic surfactants to enhance the detergency of the mixture. The surfactants compared are a 3/3/2 ratio blend of polyoxyethylene (7.5) octylphenol (OP), sodium 10 dodecylbenzene sulfonate (LAS), and polyoxyethylene (13) methylene bis(octylphenol) (MBOP). This enhanced performance is shown in Table 10, in which the total surfactant content is kept at 0.005%. The wash condition is: 150 ppm hard water, 57 ppm triethanolamine/ monoethanolamine (1/1) and 37.8°C.

15

Table 10

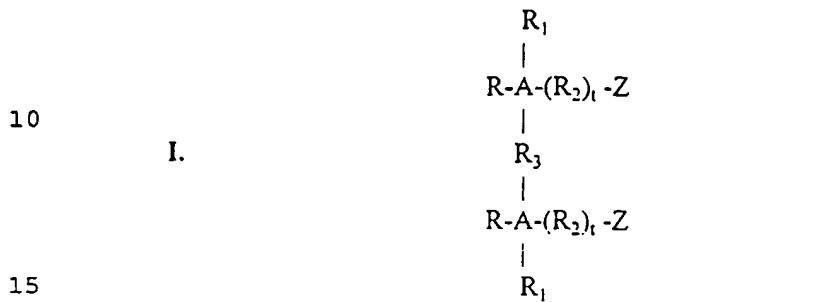
DUST-SEBUM SURFACTANTS	POLYESTER	POLYESTER/ COTTON	COTTON
Present Invention OP/LAS/MBOP (3/3/2)	20.5	23.5	17
Control: OP/LAS (1/1)	15.0	20.5	13.5

These reflectance results demonstrate that aqueous solutions containing blends of surfactants at low concentration levels, such surfactant containing 25% gemini 20 surfactants provide improved washing power over a prior art blend of conventional surfactants not containing the gemini surfactants.

This technology is very valuable to the detergent industry since it provides excellent detergency to the end-user at very low surfactant concentration use levels. Hence, it reduces overall detergent composition cost, environmental impact, and use dosage at lower temperatures. Also, using low amounts of surfactant allows effective 5 rinsing without the need of large amounts of water. Foam can be effectively monitored by working with the appropriate type and ratios of gemini to anionic and nonionic surfactants. With energy efficient washers requiring a high level of agitation and fairly low amounts of water, foam is not desirable and higher nonionic to anionic surfactant ratios are recommended. Gemini surfactants in these compositions are highly 10 desirable.

What is claimed is:

1. An aqueous surfactant composition comprising surfactant actives comprising
 5 one or more gemini surfactants of the formula:



wherein R is independently C₁ to C₂₂ alkyl, R₄C(O)-,

or R₄-B-R₅-;

wherein R₄ is C₁ to C₂₂ alkyl,

20 R₅ is C₁ to C₁₂ alkyl, and

B is -C(O)NR₆-, -NR₆-, -C(O)O-, -C(O)-, or -O(EO)_a(PO)_b- wherein a
 and b each are from 0 to 100 and a plus b is at least 1, and

R₆ is hydrogen or C₁ to C₆ alkyl;

R₁ is independently hydrogen or C₁ to C₂₂ alkyl;

25 R₂ is independently C₁ to C₁₀ alkyl, -O-, -C(O)NR₆-, -O(EO)_a(PO)_b-, -R₇-D-R--.
 or -D-R₇-D-

wherein R₇ is independently C₁-C₆ alkyl, and

D is -O-, -S-, -C(O)NR₆- or -NR₆- wherein R₆, a. and b are as defined
 above and t is independently 0 or 1;

Z is independently selected from the group consisting of hydrogen. $-\text{SO}_3\text{Y}$, $-\text{P}(\text{O})((\text{OY})_2$, $-\text{COOY}$, $-\text{CH}_2\text{COOY}$, $-\text{CH}_2\text{CH}(\text{OH})\text{CH}_2\text{SO}_3\text{Y}$. and, with the proviso that R_2 is not a polyether, $-\text{OSO}_3\text{Y}$ or $-\text{OP}(\text{O})(\text{OY})_2$,

wherein Y is hydrogen, alkali metal, alkaline earth metal, or organic

5 base salt;

A is independently $\text{C}_1\text{-C}_6$ alkyl, $-\text{O-R}_5\text{-O-}$, or aryl;

R_3 is selected from the group consisting of a bond, aryl, $\text{C}_1\text{-C}_{10}$ alkyl, $-\text{O-}$, $-\text{S-}$,

$-\text{S-S-}$, $-\text{NR}_6\text{-}$, $-\text{R}_5\text{O-}$, $-\text{R}_5[\text{O}(\text{EO})_a(\text{PO})_b]\text{-}$, $-\text{D}_1\text{-R}_8\text{-D}_1\text{-}$, and $-\text{R}_8\text{-D}_1\text{-R}_8\text{-}$

wherein R_8 is independently $\text{C}_1\text{-C}_{10}$ alkyl, $-\text{C}(\text{O})\text{-}$, $-\text{R}_5(\text{O}(\text{EO})_a(\text{PO})_b)\text{-}$,

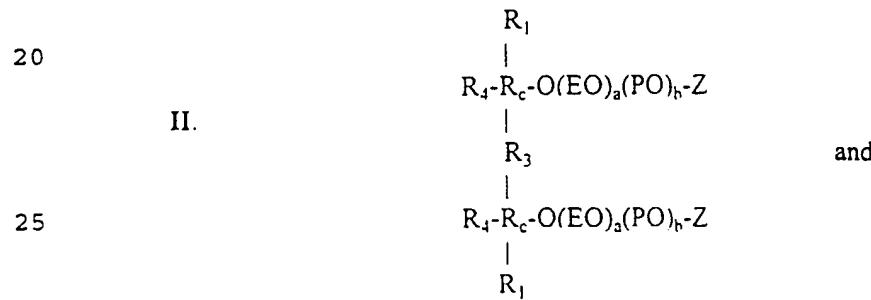
10 $-\text{O-R}_5\text{-O-}$, or aryl; and

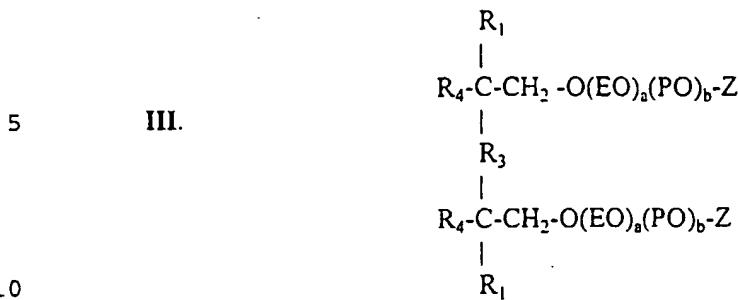
D_1 is independently $-\text{O-}$, $-\text{S-}$, $-\text{S-S-}$, $-\text{SO}_2\text{-}$, $-\text{C}(\text{O})\text{-}$, $-\text{O}(\text{EO})_a(\text{PO})_b\text{-}$, $-\text{C}(\text{O})\text{NR}_6\text{-}$,

$-\text{NR}_6\text{-}$, $-\text{O-R}_5\text{-O-}$, or aryl wherein R_5 , R_6 , a, and b are as defined above:

said composition containing a total amount of surfactant based on active weight equal to or less than about 0.01% by weight of the total weight of the composition and said 15 gemini surfactant amount comprising from about 100% to about 10% by weight of the total surfactant actives in said surfactant composition.

2. An aqueous surfactant composition comprising surfactant actives comprising one or more gemini surfactants selected from the group consisting of





wherein R_c is aryl;

R_1 is independently hydrogen or C_1 to C_{22} alkyl;

15 R_3 is selected from the group consisting of a bond, aryl, C_1 - C_{10} alkyl, -O-, -S-,

-S-S-, -NR₆-, -R₅O-, -R₅[(EO)_a(PO)_b]-, -D₁-R₈-D₁-, and -R₈-D₁-R₈-

wherein R_8 is independently C_1 - C_{10} alkyl, -C(O)-, -R₅(EO)_a(PO)_b-,

-O-R₅-O-, or aryl; and

D_1 is independently -O-, -S-, -S-S-, -SO₂-, -C(O)-, -O(EO)_a(PO)_b-, -C(O)NR₆-,

20 -NR₆-, -O-R₅-O-, or aryl wherein R_5 is C_1 - C_{12} alkyl, R_6 is hydrogen or
 C_1 - C_6 alkyl,

R_4 is C_1 to C_{22} alkyl,

Z is independently selected from the group consisting of hydrogen, -SO₃Y, -

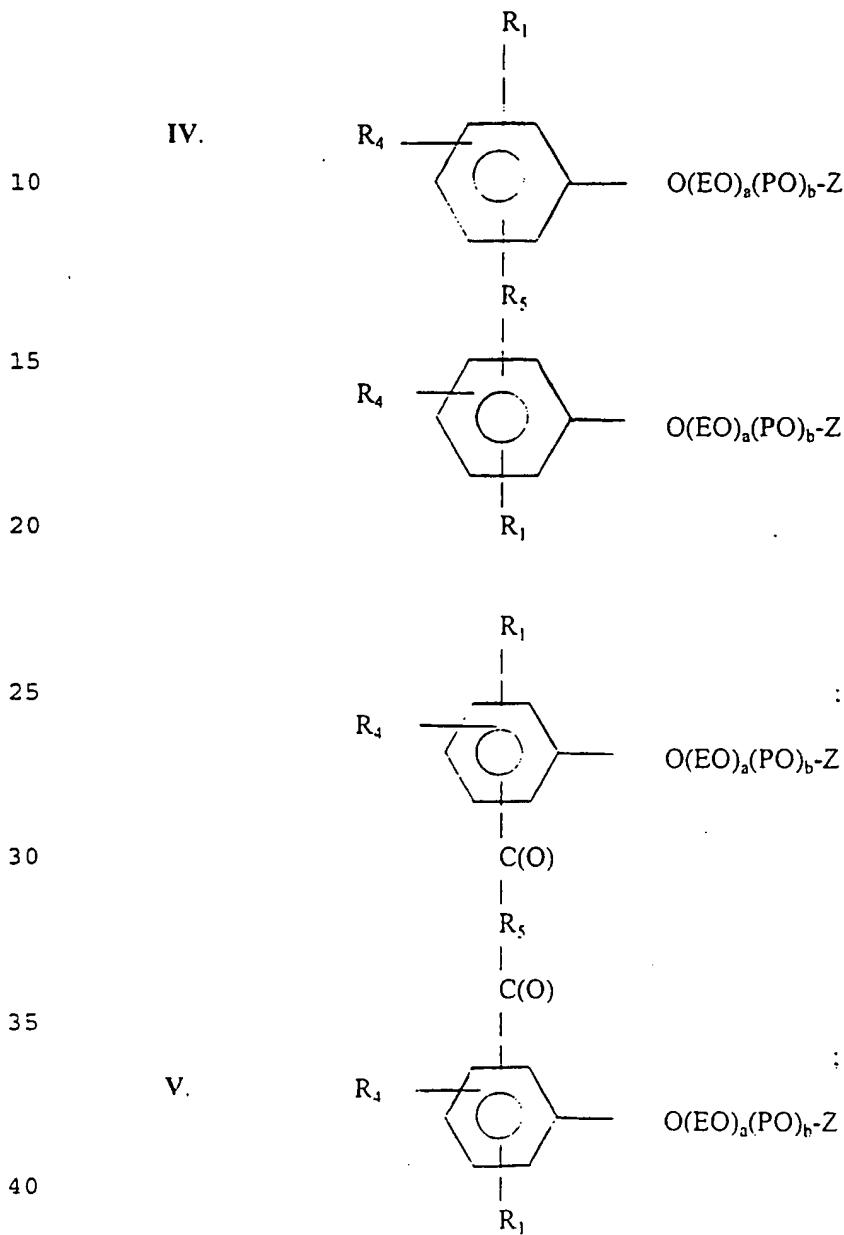
P(O)(OY)₂, -COOY, -CH₂COOY, -CH₂CH(OH)CH₂SO₃Y, and,

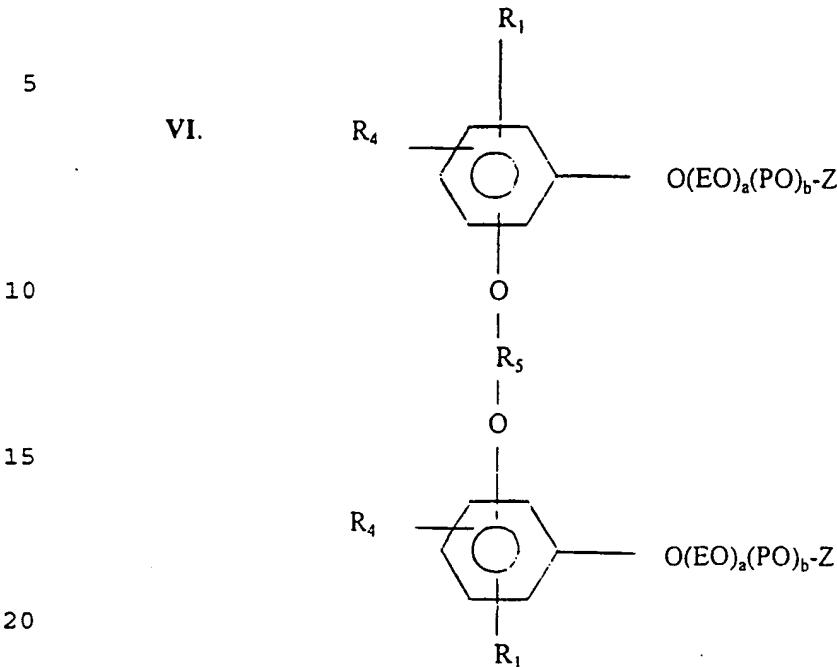
25 Y is hydrogen, alkali metal, alkaline earth metal, or organic base salt; and
a and b each are from 0 to 100 and a plus b is at least 1.

said composition containing a total amount of surfactant based on active weight equal to or less than about 0.01% by weight of the total weight of the composition and said

gemini surfactant amount comprising from about 100% to about 10% by weight of the total surfactant actives in said surfactant composition.

3. The aqueous surfactant composition of claim 2 wherein the gemini surfactant is
5 selected from the group consisting of:





wherein R₁, R₄, R₅, Z, a, and b are as herein defined.

25 4. An aqueous surfactant composition comprising surfactant actives comprising one or more gemini surfactants of the formula:



wherein

R is independently C₁ to C₂₂ alkyl, R₄C(O)-, or R₄-B-R₅-.

wherein R_4 is C_1 to C_{22} alkyl,

R_5 is C_1 to C_{12} alkyl, and

B is $-C(O)NR_6-$, $-NR_6-$, $-C(O)O-$, $-C(O)-$, or $-O(EO)_a(PO)_b-$ wherein a and b each are from 0 to 100 and a plus b is at least 1, and

5 R_6 is hydrogen or C_1 to C_6 alkyl;

R_1 is independently hydrogen, C_1 - C_{22} alkyl, or $- (EO)_a(PO)_bO-$ H ;

R_2 is independently C_1 to C_{10} alkyl, $-O-$, $-C(O)NR_6-$, $-O(EO)_a(PO)_b-$, $-R_7-D-R_7-$ or $-D-$

R_7-D- wherein R_7 is independently C_1 - C_6 alkyl, and D is $-O-$, $-S-$, $-C(O)NR_6-$, $-NR_6-$, $-C(O)-R_5-CH_2O-$, and $-NR_6-C(O)-NR_6-R_4-$.

10 R_3 is selected from the group consisting of a bond, aryl, C_1 - C_{10} alkyl, and $-R_8-D_1-R_8-$

wherein R_8 is independently C_1 - C_{10} alkyl, $-C(O)-$, $-R_5(O(EO)_a(PO)_b)-$, or aryl;

and

D_1 is $-O-$, $-S-$, $-S-S-$, $-SO_2-$, $-C(O)-$, $-O(EO)_a(PO)_b-$, $-C(O)NR_6-$, $-NR_6-$, $-O-R_5-O-$, or

aryl wherein R_5 , R_6 , a , and b are as defined above;

15 t is independently 0 or 1; and

Z is independently selected from the group consisting of hydrogen, $-SO_3Y$, $-$

$P(O)((OY)_2$, $-COOY$, $-CH_2COOY$, $-CH_2CH(OH)CH_2SO_3Y$, and, with the

proviso that R_2 is not a polyether, $-OSO_3Y$ or $-OP(O)(OY)_2$

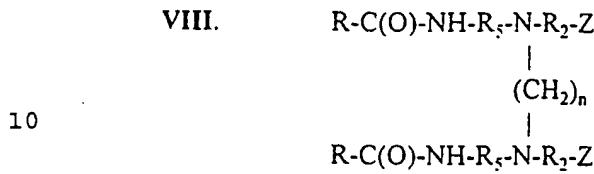
wherein Y is hydrogen, alkali metal, alkaline earth metal, or organic

20 base salt;

said composition containing a total amount of surfactant based on active weight equal to or less than about 0.01% by weight of the total weight of the composition and said

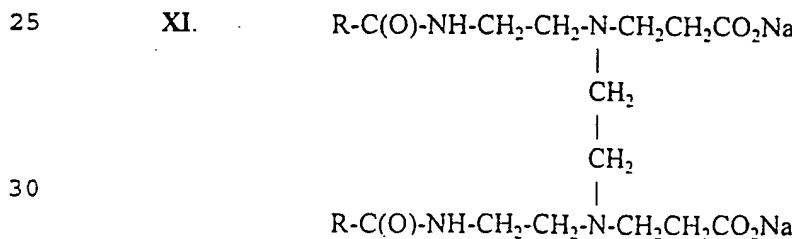
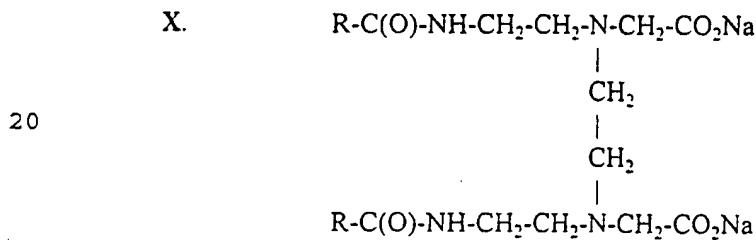
gemini surfactant amount comprising from about 100% to about 10% by weight of the total surfactant actives in said surfactant composition.

5. The aqueous surfactant composition of claim 4 wherein the gemini surfactant is
5 of the formula:

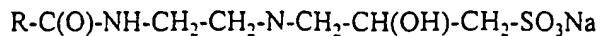


wherein R, R₂, R₅, and Z are as herein defined and n is from about 2 to about 10.

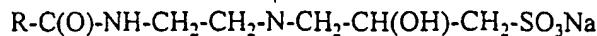
15 6. The aqueous surfactant composition of claim 5 wherein the gemini surfactant is selected from the group consisting of:



XII.



5

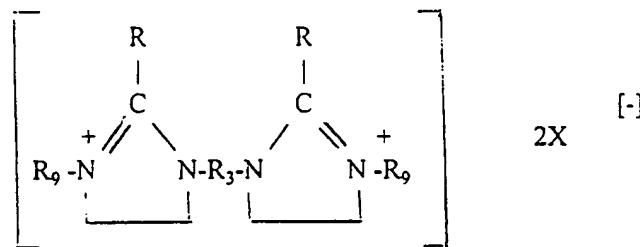


10 wherein R is as herein defined.

7. An aqueous surfactant composition comprising surfactant actives comprising one or more gemini surfactants of the formula:

15

XIII.



20

wherein R is independently C_1 to C_{22} alkyl, $\text{R}_4\text{C}(\text{O})-$,or $\text{R}_4\text{-B-}\text{R}_5-$;wherein R_4 is C_1 to C_{22} alkyl, R_5 is C_1 to C_{12} alkyl. and

25

 B is $-\text{C}(\text{O})\text{NR}_6-$, $-\text{NR}_6-$, $-\text{C}(\text{O})\text{O}-$, $-\text{C}(\text{O})-$, or $-\text{O}(\text{EO})_a(\text{PO})_b-$ wherein a and b each are from 0 to 100 and a plus b is at least 1, and R_6 is hydrogen or C_1 to C_6 alkyl; R_3 is selected from the group consisting of a bond, aryl, $\text{C}_1\text{-}\text{C}_{10}$ alkyl. and $-\text{R}_8\text{-D}_1\text{-R}_8-$

30

wherein R_8 is independently $\text{C}_1\text{-}\text{C}_{10}$ alkyl, $-\text{C}(\text{O})-$, $-\text{R}_5(\text{O}(\text{EO})_a(\text{PO})_b)-$, or aryl; and

D_1 is $-O-$, $-S-$, $-S-S-$, $-SO_2-$, $-C(O)-$, $-O(EO)_a(PO)_b-$, $-C(O)NR_6-$, $-NR_6-$, $-O-R_5-O-$, or aryl wherein R_5 , R_6 , a , and b are as defined above

R_9 is independently C_1-C_{10} alkyl or alkylaryl; and

5 X is a counterion;

said composition containing a total amount of surfactant based on active weight equal to or less than about 0.01% by weight of the total weight of the composition and said gemini surfactant amount comprising from about 100% to about 10% by weight of the total surfactant actives in said surfactant composition.

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8. An aqueous surfactant composition comprising surfactant actives comprising one or more gemini surfactants of the formula:

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XIV. $R_{13}-(CH_2)_p-N-R_{14}$



20

wherein

$R_{13}-(CH_2)_p-N-R_{14}$

R_3 is selected from the group consisting of a bond, aryl, C_1-C_{10} alkyl, and $-R_8-D_1-R_8-$

wherein R_8 is independently C_1-C_{10} alkyl, $-C(O)-$, $-R_5(O(EO)_a(PO)_b)-$, or aryl;

and

25

D₁ is -O-, -S-, -S-S-, -SO₂-, -C(O)-, -O(EO)_a(PO)_b-, -C(O)NR₆-, -NR₆-, -O-R₅-O-, or aryl wherein R₅ is C₁-C₁₂ alkyl, R₆ is hydrogen or C₁-C₆ alkyl, and a and b each are from 0 to 100 and a plus b is at least 1,

R₁₃ is a sugar moiety;

5 R₁₄ is C₁-C₂₂ alkyl or -C(O)R₄

wherein R₄ is C₁ to C₂₂alkyl; and p is independently 0 to 4;

said composition containing a total amount of surfactant based on active weight equal to or less than about 0.01% by weight of the total weight of the composition and said 10 gemini surfactant amount comprising from about 100% to about 10% by weight of the total surfactant actives in said surfactant composition.

9. An aqueous surfactant composition as recited in claim 1 wherein the amount of total surfactant is equal to or less than 80% of the cmc of the corresponding 15 conventional surfactant.

10. An aqueous surfactant composition as recited in Claim 2. wherein the amount of total surfactant is equal to or less than 80% of the cmc of the corresponding conventional surfactant.

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11. An aqueous surfactant composition as recited in Claim 4 wherein the amount of total surfactant is equal to or less than 80% of the cmc of the corresponding conventional surfactant.

12. An aqueous surfactant composition as recited in Claim 7, wherein the amount of total surfactant is equal to or less than 80% of the cmc of the corresponding conventional surfactant.

5 13. An aqueous surfactant composition as recited in Claim 8, wherein the amount of total surfactant is equal to or less than 80% of the cmc of the corresponding conventional surfactant.

14. An aqueous surfactant composition as recited in claim 1 wherein the total amount of surfactant actives is equal to or less than about 0.008% by weight.

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15. An aqueous surfactant composition as recited in claim 2 wherein the total amount of surfactant actives is equal to or less than about 0.008% by weight.

16. An aqueous surfactant composition as recited in claim 4 wherein the total amount of surfactant actives is equal to or less than about 0.008% by weight.

17. An aqueous surfactant composition of claim 7, wherein the total amount of surfactant actives is equal to or less than about 0.008% by weight.

20 18. An aqueous surfactant composition of claim 8, wherein the total amount of surfactant actives is equal to or less than about 0.008% by weight.

19. An aqueous surfactant composition as recited in claim 1 wherein the total amount of surfactant actives is equal to or less than about 0.006% by weight.

20. An aqueous surfactant composition as recited in claim 2 wherein the total amount of surfactant actives is equal to or less than about 0.006% by weight.

5 21. An aqueous surfactant composition as recited in claim 4 wherein the total amount of surfactant actives is equal to or less than about 0.006% by weight.

22. An aqueous surfactant composition as recited in claim 7 wherein the total amount of surfactant actives is equal to or less than about 0.006% by weight.

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23. An aqueous surfactant composition as recited in claim 8 wherein the total amount of surfactant actives is equal to or less than about 0.006% by weight.

24. The aqueous composition of claim 1 wherein Z is hydrogen.

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25. The aqueous composition of claim 2 wherein Z is hydrogen.

26. The aqueous composition of claim 4 wherein Z is hydrogen.

FIGURE 1

Comparison of dust-schum detergency of Gemini and conventional surfactants on different fabric at 0.005% by weight.

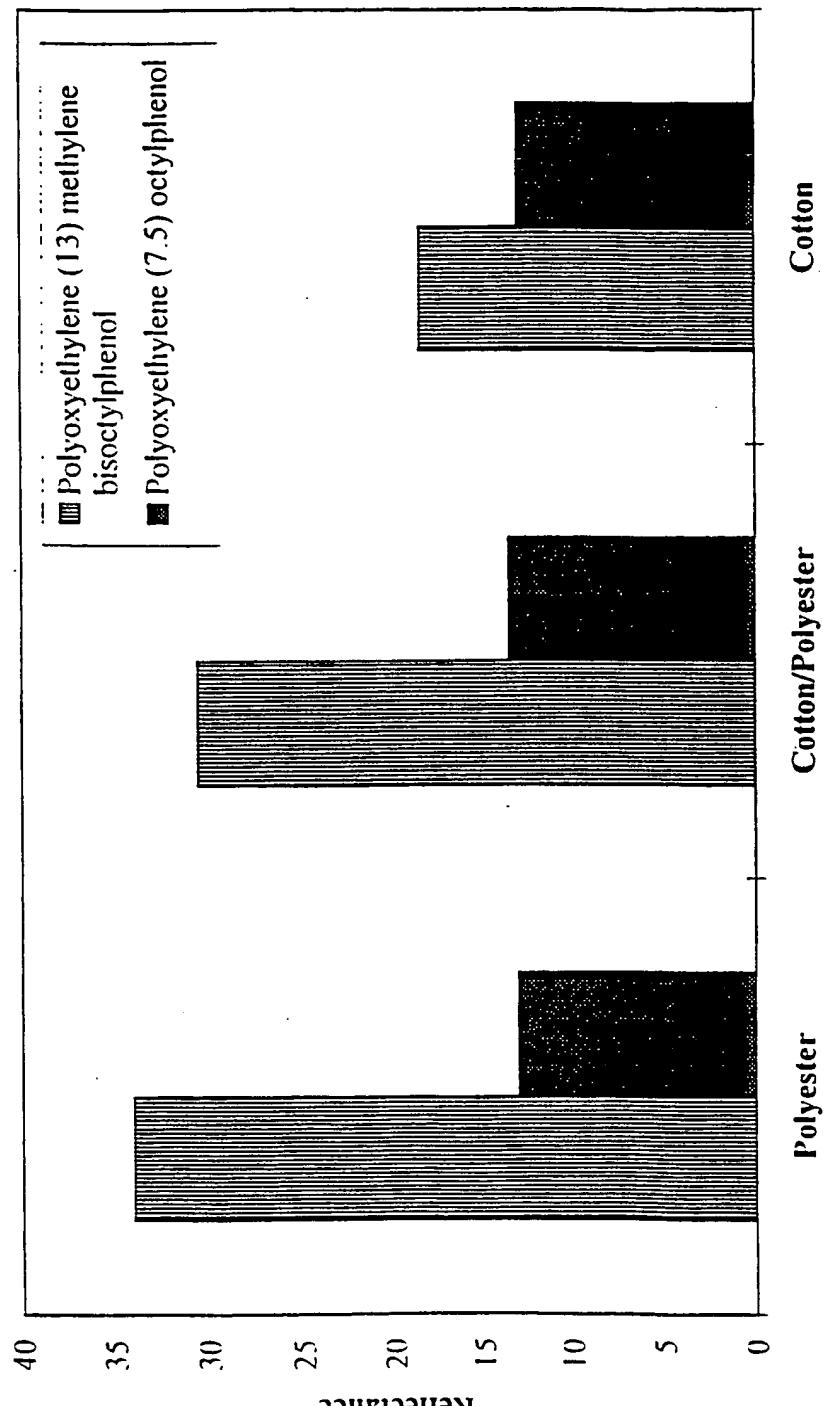


FIGURE 2

Comparison of dust-sebum detergency of Gemini and conventional surfactants on different fabric at 0.01% by weight.

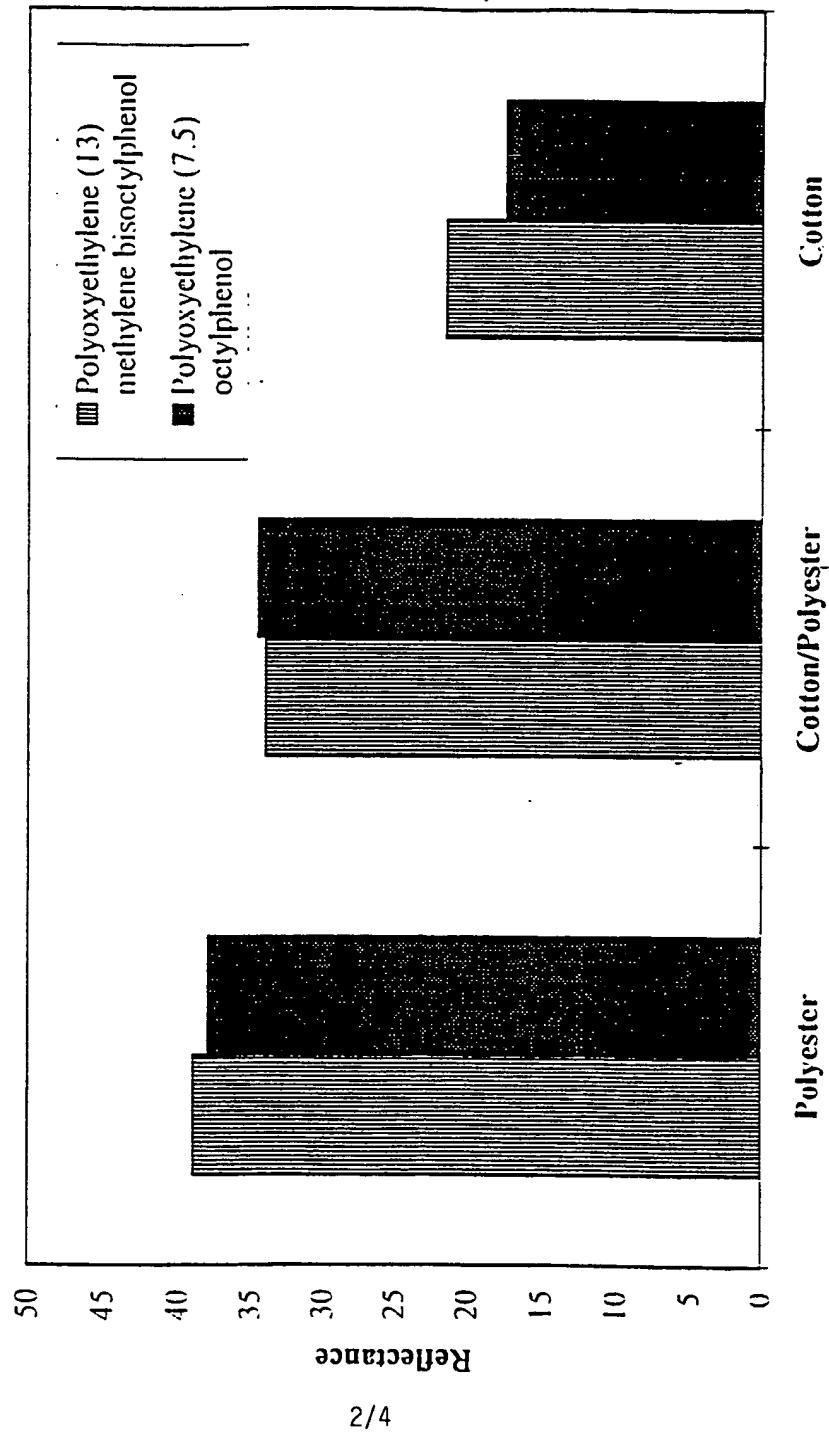


FIGURE 3

Comparison of dust-sebum detergency of different surfactant combinations on different fabric at 0.001% by weight.

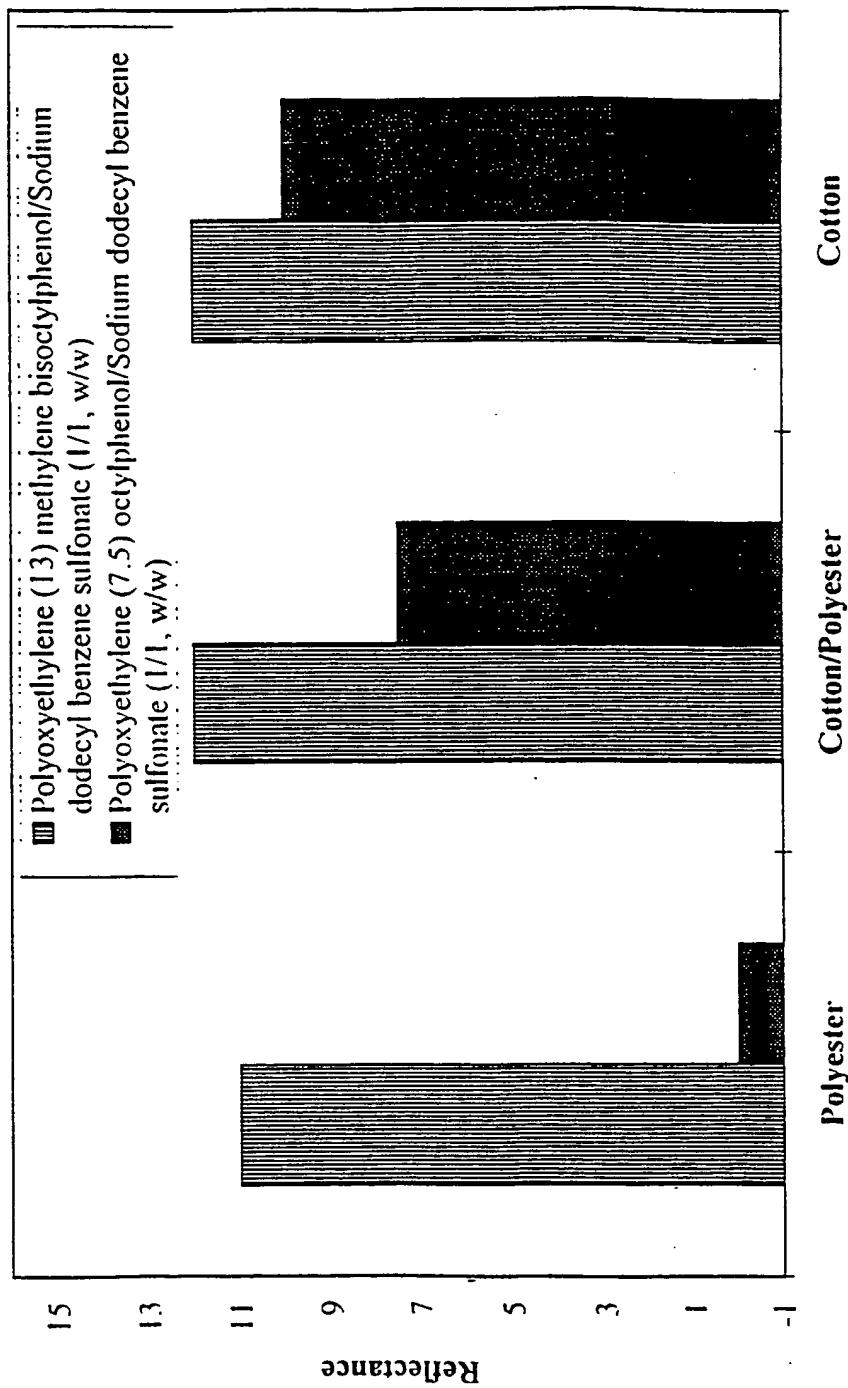
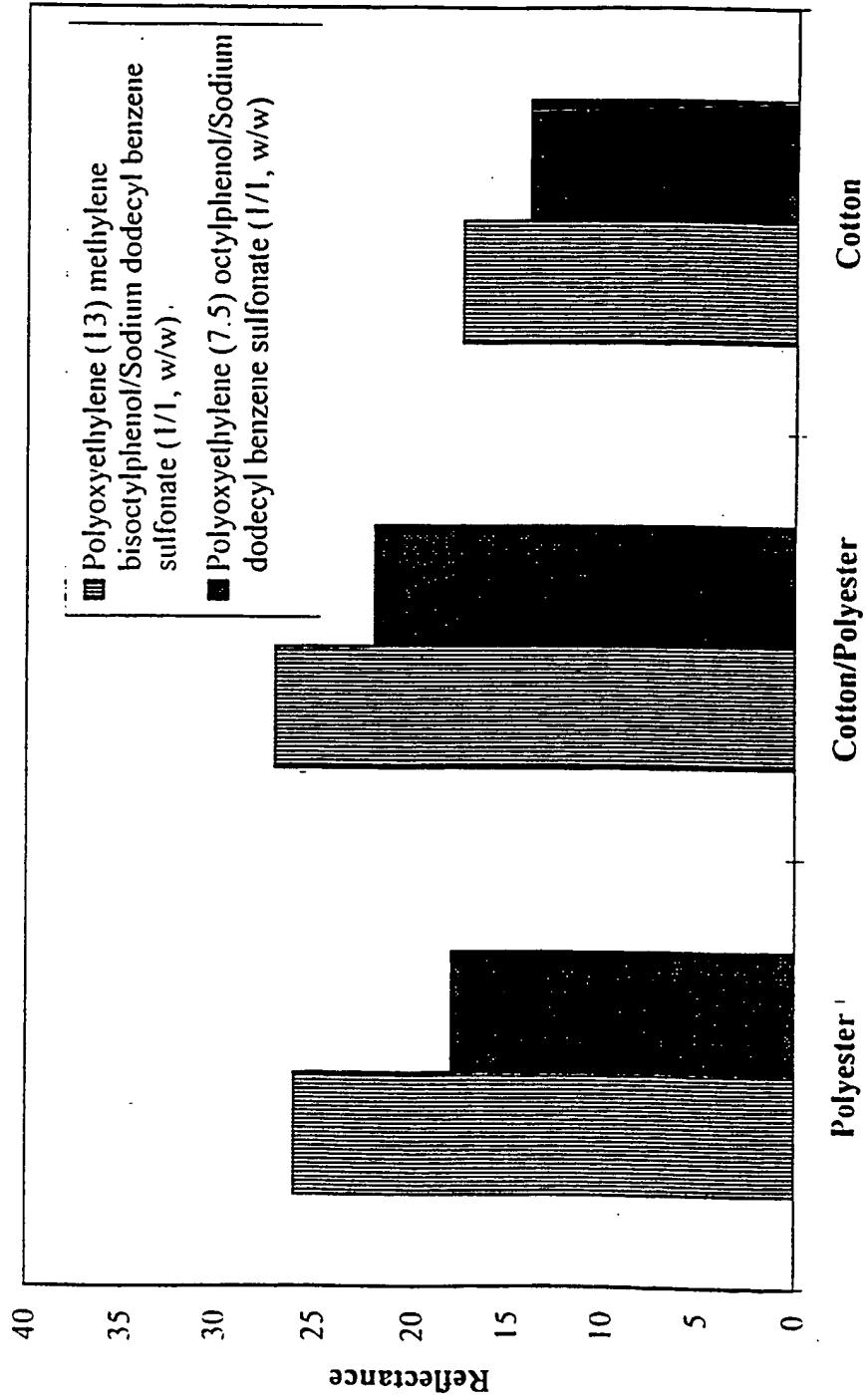


FIGURE 4

Comparison of dust-sebum detergency of different surfactant combinations on different fabric at 0.005% by weight.



INTERNATIONAL SEARCH REPORT

International Application No
PCT/IB 97/01230

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B01F17/00 C11D1/04 C11D1/12 C11D1/34

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B01F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 160 450 A (MITSUO OKAHARA ET AL) 3 November 1992 cited in the application see claims 1-18 ---	1,2,9, 10,14, 15,19, 20,24,25
X	FR 2 173 311 A (HOECHST AG) 5 October 1973 see claims 1-3 ---	1-3,9, 10,14, 15,19, 20,24,25
X	EP 0 058 384 A (HOECHST AG) 25 August 1982 see claims 1-10 ---	1-3,9, 10,14, 15,19, 20,24,25 -/-

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Date of the actual completion of the international search

Date of mailing of the international search report

27 February 1998

11/03/1998

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PCT/IB 97/01230

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 697 245 A (RHONE-POULENC INC.) 21 February 1996 see claims 1-22 ---	1,2,4-6, 9,10, 14-16, 19-21, 24-26
X	EP 0 697 244 A (RHONE-POULENC INC.) 21 February 1996 see claims 1-22 ---	4-6,11, 16,21
X	WO 95 19955 A (PROCTER & GAMBLE) 27 July 1995 see claims 1-7 ---	4,11,16, 21,26
X	WO 95 19953 A (PROCTER & GAMBLE) 27 July 1995 see claims 1-7 ---	4,11,16, 21,26
X	DE 44 41 363 A (HULS AG) 23 May 1996 see claims 1-19 ---	1,2,9, 10,14, 15,19, 20,24,25
X	DE 195 05 368 A (HULS AG) 22 August 1996 see claims 1-18 ---	4,11,16, 21,26
X	DE 44 40 328 A (HULS AG) 15 May 1996 see claims 1-19 -----	4,11,16, 21,26

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 97/01230

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5160450 A	03-11-92	NONE	
FR 2173311 A	05-10-73	CH 598338 A BE 795961 A CA 994062 A DE 2306104 A GB 1425391 A IN 138696 A JP 48099227 A NL 7302331 A US 3874891 A	28-04-78 27-08-73 03-08-76 06-09-73 18-02-76 13-03-76 15-12-73 28-08-73 01-04-75
EP 58384 A	25-08-82	DE 3104991 A BR 8200741 A CA 1184924 A DK 60982 A FI 820426 A IN 159176 A IN 156610 A IN 161179 A JP 1719521 C JP 4004306 B JP 57154146 A US 4403079 A	19-08-82 21-12-82 02-04-85 13-08-82 13-08-82 04-04-87 21-09-85 10-10-87 14-12-92 27-01-92 22-09-82 06-09-83
EP 697245 A	21-02-96	US 5643864 A BR 9503713 A CA 2155277 A CN 1127158 A JP 8103646 A	01-07-97 28-05-96 20-02-96 24-07-96 23-04-96
EP 697244 A	21-02-96	US 5656586 A BR 9503714 A CA 2155486 A CN 1123714 A JP 8103645 A	12-08-97 28-05-96 20-02-96 05-06-96 23-04-96
WO 9519955 A	27-07-95	NONE	
WO 9519953 A	27-07-95	US 5534197 A	09-07-96

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 97/01230

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 9519953 A		CA 2179709 A CN 1139425 A EP 0741773 A EP 0741692 A JP 9508121 T WO 9520026 A	27-07-95 01-01-97 13-11-96 13-11-96 19-08-97 27-07-95
DE 4441363 A	23-05-96	AU 3567795 A WO 9616033 A EP 0793647 A ZA 9509817 A	17-06-96 30-05-96 10-09-97 30-05-96
DE 19505368 A	22-08-96	AU 4173196 A WO 9625388 A EP 0809625 A	04-09-96 22-08-96 03-12-97
DE 4440328 A	15-05-96	AU 3567895 A WO 9614926 A EP 0804279 A	06-06-96 23-05-96 05-11-97

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